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BIOPHYSICAL RESEARCH

ACIDIC DEPOSITION AND THE ENVIRONMENT: A LITERATURE OVERVIEW

by:

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Kananaskis Centre for Environmental Research
The University of Calgary
Calgary, Alberta, Canada

November, 1987

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The University of Calgary
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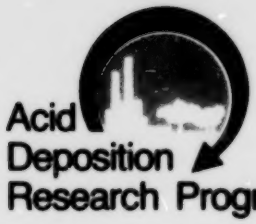

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World Literature Reviews

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ADRP-B-02-87	Visser, S., and Danielson, R. M., and Parr, J. F. 1987. **Effects of Acid-Forming Emissions on Soil Microorganisms and Microbially-Mediated Processes.** Prep for the Acid Deposition Research Program by the Kananaskis Centre for Environmental Research, The University of Calgary, Calgary, Alberta, Canada and U.S. Department of Agriculture, Beltsville, Maryland, U.S.A. 86 pp. ISBN 0-921625-04-9 (Volume 2) ISBN 0-921625-02-2 (Set of 11)
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ADRP-B-07-87	Campbell, K. W. 1987. **Pollutant Exposure and Response Relationships: A Literature Review. Geological and Hydrogeological Aspects.** Prep for the Acid Deposition Research Program by Subsurface Technologies and Instrumentation Limited, Calgary, Alberta, Canada. 152 pp. + maps. ISBN 0-921625-09-X (Volume 7) ISBN 0-921625-02-2 (Set of 11)
ADRP-B-08-87	Torn, M. S. and Degrange, J. E. and Shinn, J. H. 1987. **The Effects of Acidic Deposition on Alberta Agriculture: A Review.** Prep for the Acid Deposition Research Program by the Environmental Sciences Division, Lawrence Livermore National Laboratory. 160 pp. ISBN 0-921625-10-3 (Volume 8) ISBN 0-921625-02-2 (Set of 11)
ADRP-B-09-87	Mayo, J. M. 1987. **The Effects of Acid Deposition on Forests.** Prep for the Acid Deposition Research Program by the Department of Biology, Emporia State University. 74 pp. ISBN 0-921625-11-1 (Volume 9) ISBN 0-921625-02-2 (Set of 11)
ADRP-B-10-87	Krupa, S. V. and Kickert, R. N. 1987. **An Analysis of Numerical Models of Air Pollutant Exposure and Vegetation Response.** Prep for the Acid Deposition Research Program by the Department of Plant Pathology, University of Minnesota, St. Paul, Minnesota, U.S.A., and Consultant, Corvallis, Oregon, U.S.A. 113 pp. ISBN 0-921625-12-X (Volume 10) ISBN 0-921625-02-2 (Set of 11)
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PREFACE

The Alberta Government/Industry Acid Deposition Research Program (ADRP) is a scientific investigation designed to answer specific questions regarding the environmental effects of acidic and acid forming substances on the ecosystems of Alberta in both the short and longer terms. As part of this study, a detailed and comprehensive literature review of each of the identified critical areas of ecosystem concern was completed. The following document is intended to provide an overview on the key findings of each of these documents in both a world (Part I) and an Alberta (Part II) context.

The documents that form the basis of this synthesis are:

ADRP-B-01/87: SURFACE WATER ACIDIFICATION LITERATURE REVIEW. Prep. for the Acid Deposition Research Program by S.A. Telang, Kananaskis Centre for Environmental Research, The University of Calgary, Alberta, Canada. 132 pp. ISBN 0-921625-03-0 (Volume 1).

ADRP-B-02/87: EFFECTS OF ACID-FORMING EMISSIONS ON SOIL MICROORGANISMS AND MICROBIALLY-MEDIATED PROCESSES. Prep. for the Acid Deposition Research Program by S. Visser, R.M. Danielson, and J.F. Parr, Kananaskis Centre for Environmental Research, The University of Calgary, and U.S. Department of Agriculture, Beltsville, Maryland. 86 pp. ISBN 0-921625-04-9 (Volume 2).

ADRP-B-03/87: ENVIRONMENTAL SULPHUR ISOTOPE STUDIES IN ALBERTA: A REVIEW. Prep. for the Acid Deposition Research Program by H.R. Krouse, Department of Physics, The University of Calgary, Calgary, Alberta, Canada. 89 pp. ISBN 0-92165-06-5 (Volume 3).

ADRP-B-04/87: CRITICAL REVIEW OF INORGANIC SULPHUR MICROBIOLOGY WITH PARTICULAR REFERENCE TO ALBERTA SOILS. Prep. for the Acid Deposition Research Program by E.J. Laishley and R. Bryant, Department of Biology, The University of Calgary, Calgary, Alberta, Canada. 50 pp. ISBN 0-921625-06-5 (Volume 4).

ADRP-B-05/87: EFFECTS OF ACID DEPOSITION ON SOILS IN ALBERTA. Prep. for the Acid Deposition Research Program by L.W. Turchenek, S.A. Abboud, C.J. Tomas, R.J. Fessenden, and N. Holowaychuk, Alberta Research Council, Edmonton, Alberta. 202 pp. ISBN 0-921625-07-3 (Volume 5).

ADRP-B-06/87: MAJOR BIOPHYSICAL COMPONENTS OF ALBERTA. Prep. for the Acid Deposition Research Program by D.R. Jaques, Ecosat Geobotanical Surveys Inc., North Vancouver, British Columbia, Canada. 101 pp. + 4 maps. ISBN 0-921625-08-1 (Volume 6).

ADRP-B-07/87: POLLUTANT EXPOSURE AND RESPONSE RELATIONSHIPS: A LITERATURE REVIEW. GEOLOGICAL AND HYDROGEOLOGICAL ASPECTS. Prep. for the Acid Deposition Research Program by K.W. Campbell, Subsurface Technologies and Instrumentation Limited, Calgary, Alberta, Canada. 151 pp. + 2 maps. ISBN 0-921625-09-X (Volume 7).

ADRP-B-08/87: THE EFFECTS OF ACIDIC DEPOSITION ON ALBERTA AGRICULTURE. Prep. for the Acid Deposition Research Program by M.S. Torn, J.E. Degrange, and J.H. Shinn, Lawrence Livermore National Laboratory, California, USA. 160 pp. ISBN 0-921625-10-1 (Volume 8).

ADRP-B-09/87: THE EFFECTS OF ACID DEPOSITION ON FORESTS. Prep. for the Acid Deposition Research Program by J.M. Mayo, Department of Biology, Emporia State University, Emporia, Kansas, USA and the Kananaskis Centre for Environmental Research, The University of Calgary, Alberta, Canada. 74 pp. ISBN 0-921625-11-1 (Volume 9).

ADRP-B-10/87: AN ANALYSIS OF NUMERICAL MODELS OF AIR POLLUTANT EXPOSURE AND VEGETATION RESPONSE. Prep. for the Acid Deposition Research Program by S.V. Krupa and R.N. Kickert, Department of Plant Pathology, University of Minnesota, St. Paul, Minnesota, USA and Consultant, Corvallis, Oregon, USA. 113 pp. ISBN 0-921625-12-X (Volume 10).

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PART I.

GENERAL OVERVIEW AND WORLD PERSPECTIVE:

ACIDIC DEPOSITION AND ECOSYSTEM EFFECTS

1. INTRODUCTION TO ATMOSPHERIC CHEMISTRY AND ACIDIC DEPOSITION PROCESSES

The short- and long-term observed and/or predicted, adverse impacts of air pollutants on terrestrial and aquatic ecosystems are of utmost concern at this time (U.S. National Research Council 1983; U.S. Environmental Protection Agency 1983). Air pollutants occur as gases, vapours, and particulate matter (both dry and wet). Once pollutants are emitted, the atmosphere serves as a medium for their dilution, transport, chemical reaction, and deposition. These processes are governed by the physical and chemical properties of the pollutant emitted, its reactivity with the other constituents in the atmosphere, and by the meteorological conditions. In the end, primary and secondary pollutants are transferred from the atmosphere to surfaces (crops, forests, soils, surface waters, and materials) by dry and wet deposition.

Dry deposition may be defined as the direct collection of gaseous and particulate species on land and surface waters (Garland 1978). On the other hand, wet deposition comprises the incorporation of the pollutant in cloud droplets (rainout) and removal by falling precipitation (washout). The relative importance of the two deposition processes is known to vary in time and space (U.S. National Research Council 1983). Thus, any observed or predicted receptor responses are considered to be due to the joint action of both dry and wet deposition (Legge and Krupa 1986).

What follows in the subsequent sections of this "Introduction" was essentially extracted from Krupa et al. (1987a).

1.1 ATMOSPHERIC PROCESSES

The occurrence of "acidic precipitation" is of much concern. The acidity of precipitation, particularly in the industrialized areas, is considered to be due to the presence of strong mineral acids in the atmosphere (Hutchinson and Havas 1980; International Electric Research Exchange 1981; U.S. National Research Council 1983; U.S. Environmental Protection Agency 1983; and U.S. National Research Council 1986).

The combustion of sulphur-containing fossil fuels leads to the emission of sulphur dioxide (SO_2). Once emitted, depending upon meteorological and other conditions, a highly variable portion of the SO_2 is continuously (except during precipitation events) deposited on to surfaces by dry deposition. Particularly during the daylight hours, SO_2 is also oxidized in the emission plume and ambient atmosphere to sulphuric acid (H_2SO_4), aerosols, or sulphates by reactions occurring in the gas phase, in the liquid phase, on the surfaces of solids, or through combinations of all three (Finlayson-Pitts and Pitts 1986). For details of the SO_2 oxidation mechanisms, the reader is referred to Finlayson-Pitts and Pitts (1986), Hidy and Mueller (1986), and U.S. National Research Council (1983).

In power plant plumes, SO_2 oxidation rates of up to 4% h^{-1} have been reported (Husar et al. 1978). Often such rates are much higher if the plume passes through clouds or fog banks (Eatough et al. 1984). Similarly, the rates of production of sulphate (SO_4^{2-}) from SO_2 are much higher during the summer compared with the winter (Richards et al. 1981). According to Gillani (1978) and Forrest et al. (1981), noontime SO_2 conversion rates in a power plant plume were 1-4% h^{-1} compared with night-time rates of <0.5% h^{-1}. However, significant SO_4^{2-} production (4.5 to 10.8% h^{-1}) can occur at night-time if clouds are a contributing factor in the SO_2 conversion (Cass and Shair 1984). For

details of the suggested mechanisms for the aqueous oxidation of SO_2, the reader is referred to Graedel and Goldberg (1983), Bielski et al. (1985), and Graedel et al. (1986).

Compared with SO_2, the oxidation of the oxides of nitrogen (NOx) in power plant plumes and in ambient air is relatively less understood. In power plant plumes, rates of conversion of NOx from roughly 0.2 to 12% h^{-1} have been observed, with the rates being much greater during midday than at night (Hegg and Hobbs 1979; Richards et al. 1981). The products of NOx oxidation appear to be peroxyacetyl nitrate (PAN) and nitric acid (HNO_3), with a lesser amount of particulate nitrates (NO_3^-). In urban plumes, rates of conversion of NOx of <5% h^{-1} to 24% h^{-1} have been reported (Chang et al. 1979; Spicer 1982a,b).

In the atmosphere, H_2SO_4 and HNO_3 differ in their physical and chemical behaviour. Nitric acid is more volatile and thus, significant concentrations of that substance can exist in the gas phase. On the other hand, H_2SO_4 has a low vapour pressure under ambient conditions and exists in the fine particle phase (<2.0 μm) (Whitby 1978; Roedel 1979). These particles, in addition to causing visibility degradation, can also act as cloud condensation nuclei (Husar et al. 1978).

Both H_2SO_4 and HNO_3 can react with bases present in the atmosphere to form salts. For example, H_2SO_4 can react rapidly with ammonia (NH_3) in the atmosphere to form ammonium acid sulphate (NH_4HSO_4), letovicite ($(NH_4)_3H(SO_4)_2$), and ammonium sulphate ($(NH_4)_2SO_4$). Similarly, HNO_3 can react with NH_3 to form ammonium nitrate (NH_4NO_3). Because of the characteristics of the equilibrium between HNO_3, NH_3, and NH_4NO_3, HNO_3 can revolatilize relatively easily even after forming the ammonium salt (Finlayson-Pitts and Pitts 1986). No such analogous physical and chemical changes exist for H_2SO_4. In addition to the ammonium salts, H_2SO_4 and HNO_3 can readily form salts with other cations, such as Ca^{2+}, Mg^{2+}, and so forth.

1.2 DEPOSITION PROCESSES

According to Garland (1978) deposition processes limit the lifetime of sulphur and other pollutants in the atmosphere, control the distance travelled before deposition, and limit their atmospheric concentrations. Therefore, an understanding of such processes is essential for a proper assessment of the environmental significance of natural and man-made emissions of sulphur and other pollutants.

Dry deposition leads to the direct collection of gases, vapours, and particles on land and water surfaces. This pollutant transfer process includes diffusion, Brownian motion, interception, impaction, and sedimentation (U.S. National Research Council 1983; Legge and Krupa 1986; and Voldner et al. 1986). The rate at which these processes transfer pollutants from the air to exposed surfaces is controlled by a wide range of chemical, physical, and biological factors which vary in their relative importance according to the nature and state of the surface, the characteristics of the pollutant, and the state of the atmosphere (U.S. National Research Council 1983). The complexity of the individual processes involved and the variety of possible interactions among them combine to prohibit easy generalization; nevertheless, a "deposition velocity" v_d, analogous to a gravitational falling speed, is of considerable use. In practice, knowledge of v_d enables fluxes, F, to be estimated from air concentrations, C, as the simple product, $v_d \cdot C$ (U.S. National Research Council 1983).

For more information on the dry deposition of air pollutants, the reader is referred to Garland (1978), International Electric Research Exchange (1981), U.S. National Research Council (1983), and Chamberlain (1986).

Both SO_2 and SO_4^{2-} can contribute significantly to the dissolved sulphur in rain. The contribution of SO_4^{2-} appears inevitable, since SO_4^{2-} particles serve as cloud condensation nuclei. On the other hand, the incorporation of SO_2 may be suppressed if the condensation nuclei are acidic. Dana et al. (1975) imply no more than 3% deposition in rain from a power plant plume in the first 10 km. Larson et al. (1975) deduced that only 8% of the sulphur emitted from a smelter while rain was falling was deposited within 60 km. Garland (1978) has summarized the information on mechanisms contributing to sulphur in rainwater.

In addition to the rainout of condensation nuclei, several other physical processes may contribute to sulphate in rain. Diffusiophoresis and Brownian diffusion may result in the collection of small particles on to the cloud droplets and raindrops may further collect particles by impaction, interception, or diffusion. According to Garland (1978) only the rainout of condensation nuclei appears capable of explaining the concentrations of several mg L^{-1} of SO_4^{2-} observed in practice.

The washout of large particles by raindrops may make a significant contribution, but this fraction of the aerosol will be exhausted by the first few millimetres of rain and may, therefore, account for the enhancement in sulphate concentration observed at the beginning of some periods of rain (Meurrens 1974; Pratt et al. 1983).

Diffusion and interception may be of greater significance in snow because of the larger surface area of the precipitation elements. In addition, the concentration of condensation nuclei collected in precipitation may be much reduced if distillation from liquid to solid phase dominates the aggregation of cloud droplets in the growth of snowflakes.

In summary, the probable contribution to acidity of dissolved SO_2 is smaller than the contribution due to the rainout of SO_4^{2-}. However, oxidation of SO_2 in clouds can make a substantial contribution to the SO_4^{2-} in rain.

In contrast to SO_4^{2-}, much less information has been published regarding the removal mechanisms of nitrogen species by precipitation. There is some evidence for the formation of HNO_3 in clouds and rainwater. Recently, both theory and experimental evidence suggest that HNO_3 may be formed rapidly from a combined gas phase/liquid phase process (U.S. National Research Council 1983). Although significant uncertainty remains concerning the source of HNO_3 in clouds and rainwater, the limited evidence currently available favours the probable importance of the formation of nitrogen pentoxide (N_2O_5) from nitrogen dioxide (NO_2), followed by its reaction with water droplets to form HNO_3 (Finlayson-Pitts and Pitts 1986). It also appears that HNO_3 can be effectively scavenged by precipitation.

1.3 THE CHEMISTRY OF PRECIPITATION

Because of the significant concern arising from the occurrence of "acidic precipitation", numerous investigators have examined the qualitative and quantitative aspects of precipitation chemistry in the last 15-20 years. For more details than those presented in the following section, the reader is referred to Husar et al. (1978),

Chamberlain et al. (1981), U.S. National Research Council (1983), Teasley (1984), and U.S. National Research Council (1986).

In comparison with seawater (Whitfield 1979), precipitation can be considered as a highly unbuffered, dilute solution of organic and inorganic ions. Precipitation is also composed of an insoluble fraction consisting of organic (e.g., pollen, pesticides, and so forth) and inorganic (e.g., crustal) coarse (>2.0 μm size) particles (Krupa et al. 1976). However, it is the soluble fraction which is of concern in the context of "acidic precipitation". Table 1 lists some of the inorganic ions important in precipitation chemistry. Ecological effects scientists have utilized the concentrations of many of these ions together with precipitation depth to compute ion deposition ($kg.ha^{-1}$) in order to evaluate effects (U.S. Environmental Protection Agency 1983).

Table 1. Some inorganic ions important in precipitation chemistry.*

Cations	Anions
H^+	
NH_4^+	Cl^-
Na^+	NO_3^-
K^+	SO_3^{2-}
Ca^{2+}	SO_4^{2-}
Mg^{2+}	PO_4^{2-}
	CO_3^{2-}

* All ions are presented here in their completely dissociated states. The reader should note, however, that various states of partial dissociation are possible as well (e.g., HSO_3^-, HCO_3^-).

Source: U.S. National Research Council (1983).

The pH of natural precipitation is often assumed to be regulated by the dissociation of dissolved carbon dioxide (CO_2), thus having a value of 5.6. Precipitation pH values below 5.6 are therefore assumed to be due to the addition of acidic components (primarily related to SO_4^{2-} and NO_3^-) by human activity (Garrels and Mackenzie 1971; Likens and Bormann 1974; and Galloway et al. 1976).

According to some investigators, the acidity and concentrations of SO_4^{2-} and NO_3^- and some other components in precipitation have increased in recent years in certain geographic locations as a result of human activities (Cogbill and Likens 1974; Galloway et al. 1976; Martin and Barber 1977; and Likens and Butler 1981).

The data from Hubbard Brook, New Hampshire revealed several trends (Likens et al. 1980) which were supported at least qualitatively by bulk deposition monitoring data (but which had relatively unreliable quality control) from nine sites in New York State (Miles and Yost 1982; Peters et al. 1982). These trends indicated that:

1. There has been a decrease in SO_4^{2-} concentration since 1964 but an increase in NO_3^- concentration over the same time;
2. The annual pH of precipitation showed no long-term, significant change from 1964 to 1977, although several short-term changes did occur;
3. A linear regression equation of data points from 1964 to 1977 indicated no statistically significant trends in H^+ deposition; and
4. Recent changes in H^+ deposition correspond more with changes in NO_3^- deposition than with SO_4^{2-} deposition, even though H_2SO_4 is the dominant species at Hubbard Brook. The contribution of NO_3^- to total acidity has been increasing, whereas that of SO_4^{2-} has been decreasing (Galloway and Likens 1981). Year-to-year changes superimposed on the long-term trend may be related to climatological influences (U.S. National Research Council 1983).

According to Hansen et al. (1981) available data are not of sufficient quantity and quality to support any long-term trends in precipitation acidity change over the past 50 years in the eastern United States. However, the observations do show that precipitation is definitely acidic over this region, and is probably more acidic than expected from natural baseline conditions.

Recently, Schertz and Hirsch (1985) performed a trend analysis (1978-1983) of data from 19 sites of the NADP (National Atmospheric Deposition Program). They concluded that 41% of the trends detected in the ion concentrations were downward trends, 4% were upward trends, and 55% showed no trends at $\alpha = 0.2$. The authors also concluded that the two constituents of greatest interest in terms of human-generated emissions and environmental effects, SO_4^{2-} and NO_3^-, showed only downward trends, and SO_4^{2-} showed the largest decreases in concentration per year of all the ions tested.

On the other hand, Stensland et al. (1986) in their analysis of long-term trends, derived the following conclusions:

1. The eastern half of the United States experiences concentrations of SO_4^{2-} and NO_3^- in precipitation that are, in general, greater by at least a factor of five than those in the remote areas of the world, indicating that levels have increased by this amount in northeastern North America since sometime before the 1950's;
2. Data on the chemistry of precipitation before 1955 should not be used for trend analysis;
3. Precipitation is currently more acidic in parts of the eastern United States than it was in the mid-1950's or mid-1960's; however, the amount of change and its mechanism are in dispute;
4. Precipitation SO_4^{2-} concentrations and possibly acidity have increased in the southeastern United States since the mid-1950's; and
5. In general, individual sites or groups of a few neighboring sites cannot be assumed 'a priori' to provide regionally representative information; regional representativeness must be demonstrated on a site-by-site basis.

Assuming that acidity has increased (at least in certain locations) and that SO_2 and NOx are responsible for most of the free acidity, a strong statistical relationship should be observed between H^+ and SO_4^{2-} and/or NO_3^-. Information to date suggests that the degree of association is site specific and that proximity to sources of SO_2 and NOx, as well as to sources of other substances, may influence the chemical nature of acidic substances in the atmosphere (Lefohn and Krupa 1984). At a given site, differences in the meteorology between events may result in wide variations in the measured acidity, concentrations of SO_4^{2-} and NO_3^-, and correlations between these ions (Pratt et al. 1984; Pratt and Krupa 1985). Sequeira (1982) found correlation coefficients in excess of 0.8 between SO_4^{2-} and H^+ at Mauna Loa, Hawaii, somewhat lower values at Monte Cimone, Italy, and 0.01 at Alamosa, Colorado. Barrie (1981) examined summer data from eastern Canadian sites and found correlation coefficients (r^2 values) between SO_4^{2-} and H^+ as high as 0.99 at some sites and as low as -0.39 at other sites. Similarly, Pratt et al. (1983), examining four years of rainfall chemistry at seven sites in a 600 km^2 area in central Minnesota, found correlation coefficients between SO_4^{2-} and H^+ to vary from r^2 values of 0.15 to 0.42, and between NO_3^- and H^+ from 0.06 to 0.62.

Kasina (1980) found no significant correlation between acidity and SO_4^{2-} in southern Poland. On the other hand, Madsen (1981) found good correlations between H^+ and excess SO_4^{2-} on the east coast of Florida during most of the months from late 1977 to late 1979. McNaughton (1981) found correlation coefficients in excess of 0.7 for all MAP3S/RAINE (1982) sites except Illinois, where the value was below 0.4.

The preceding discussion shows the complexity in generalizing the characteristics of precipitation chemistry because of significant spatial variability. In addition, it is well known that precipitation chemistry exhibits distinct temporal variability including seasonality (Pratt and Krupa 1983; Dana and Easter 1987). For example, Bowersox and de Pena (1980) concluded, by applying multiple linear regression analysis for a central Pennsylvania site, that on average H_2SO_4 was the principal contributor to H^+ concentration in rain, but that the acidity in snow was principally from HNO_3.

According to Sequeira (1982), the pH of atmospheric precipitation at a given location depends on the chemical nature and relative proportions of acids and bases in the solution. Sequeira concluded that a pH of 5.6 may not be a reasonable reference value for unpolluted precipitation. Charlson and Rodhe (1982) also questioned the validity of using pH 5.6 as the background reference point, citing naturally occurring acids as possibly responsible for low pH values of rain. They stated that consideration of the natural cycling of water and sulphate through the atmosphere, precipitation rates, and experimentally determined rates of SO_4^{2-} scavenging indicates that average pH values of approximately 5.0 would be expected in pristine locations in the absence of basic materials. This value will vary considerably due to the variability in scavenging efficiencies as well as geographic patchiness in the sulphur and hydrological cycles. Thus, precipitation pH values might range from 4.5 to 5.6 due to these variabilities alone (Charlson and Rodhe 1982). Recently, Lefohn and Krupa (1987) found that pH of precipitation with minimum concentrations of SO_4^{2-} and NO_3 was in the range of 4.6 to 5.5 for the northeast United States.

An aspect of precipitation chemistry which has been largely ignored until recently is the presence of organic acids (Krupa et al. 1976). Meyers and Hites (1982), Kawamura and Kaplan (1983), Keene and Galloway (1984), Guiang et al. (1984), and Chapman et al. (1986) have all shown the presence of organic acids in precipitation. Keene and Galloway (1984) estimated that organic acids may contribute 16 to 35% of the volume weighted free acidity in precipitation of North America. Krupa et al. (1987b) calculated theoretical precipitation H^+ concentrations for Minnesota, based on the assumption that all of the organic anions were present as the corresponding acids. A plot of the calculated versus the measured H^+ concentrations showed poor correlation, yet the mean calculated and the mean measured H^+ concentrations were nearly equal, on a yearly basis. The weak organic acids could account for all of the deposited acidity.

Independent of these considerations of the complexity of precipitation chemistry, it is widely accepted that SO_4^{2-} and NO_3^- form the basis for acidic precipitation (U.S. National Research Council 1983). Statistical parameters such as the mean and standard deviation, which can be interpreted unambiguously when the distribution of data is normal or Gaussian, do not accurately characterize the observed distributions of precipitation ions (Knapp et al. 1987). These distributions appear to be best described by the mathematical functions of the Weibull family (Nosal and Krupa 1986).

Numerous investigators have used linear or linearizable statistical methods in evaluating the relationships between the major inorganic ions in precipitation. The use of such techniques assumes that: (1) the data are normally distributed and independent; and (2) the residuals in the regression are normally distributed, independent, unbiased, and homoscedastic (Snedecor and Cochran 1978). Recently, Nosal and Krupa (1986) showed that the aforementioned assumptions are violated by the data on precipitation chemistry. An additional implication of this finding is that precipitation data between sites cannot be pooled or combined in performing parametric statistical analyses of either the precipitation characteristics or acidic precipitation-receptor response relationships.

1.4 WET DEPOSITION IN ALBERTA

Since the early 1970's, several investigators have studied the precipitation composition and wet deposition in Alberta (Nyborg et al. 1977; Caiazza et al. 1978; Klemm and Gray 1982; Lau 1985; and Lau and Das 1985). Based on a study during 1973-1974, Nyborg et al. (1977) concluded that rain and snow in Alberta were seldom acidic. Klemm and Gray (1982), in their study during 1977-1978, found that less than 20% of the pH values of precipitation in central Alberta were below 5.0 and none were below 4.0. According to Lau and Das (1985) volume weighted average pH values of composite monthly precipitation samples at 11 Alberta CANSAP (Canadian Network for Sampling Precipitation) stations during 1978-1984 ranged between 5.17 and 6.06 (Table 2). Wet deposition of H^+ (kg ha^{-1} y^{-1}) in Alberta during 1978-1982 was 24 times less compared with the values for Ontario, Quebec, and Nova Scotia (Table 3). In a similar comparison, SO_4^{2-} deposition in Alberta was 1.7 to 3.7 times less and NO_3^- deposition was 1.8 to 6.0 times less compared with the three eastern states (Table 3). Kociuba (1984) based on modelling concluded that dry deposition of sulphate was much greater than wet deposition at all but one CANSAP sampling site in Alberta (Table 4). In validating the model

Table 2. Wet deposition in Alberta (1978-1984).

Station	Average Annual Deposition (mole m^{-2} y^{-1})			Average pH
	Sulphate	Nitrate	Hydrogen Ion	
Beaverlodge	6.8	4.7	3.2	5.17
Calgary	12.8	8.1	0.7	5.77
Coronation	7.4	6.3	1.3	5.46
Edmonton	8.1	6.8	1.5	5.45
Edson	9.0	4.8	3.1	5.26
Ft. McMurray	8.1	4.8	1.0	5.61
Lethbridge	10.5	10.8	0.4	6.06
Red Deer	8.8	7.4	2.0	5.39
Rocky Mountain House	9.9	6.0	1.5	5.53
Suffield	8.8	6.9	0.8	5.60
Whitecourt	11.4	6.9	1.1	5.71
Alberta Average	9.2	6.7	1.5	5.48

sulphate: 1 mole m^{-2} = 0.961 kg ha^{-1}
nitrate: 1 mole m^{-2} = 0.620 kg ha^{-1}
hydrogen ion: 1 mole m^{-2} = 0.010 kg ha^{-1}

From: Lau and Das (1985)

Table 3. Wet deposition of H^+, SO_4^{2-}, and NO_3^- (kg ha^{-1} y^{-1}) in Alberta and at selected Canadian stations from 1978 to 1982.*

Location	Ion		
	H^+	SO_4^{2-}	NO_3^-
Beaverlodge (Alta.)	0.031	6.8	3.2
Calgary (Alta.)	0.004	15.5	5.8
Coronation (Alta.)	0.011	8.0	4.6
Edson (Alta.)	0.33	9.0	3.1
Fort McMurray (Alta.)	0.010	8.0	3.6
Lethbridge (Alta.)	0.003	11.5	7.6
Red Deer (Alta.)	0.022	9.4	5.2
Rocky Mtn. House (Alta.)	0.013	10.3	3.7
Suffield (Alta.)	0.009	9.9	4.6
Whitecourt (Alta.)	0 015	10.5	4.3
Prince George (B.C.)	0.009	10.6	3.1
Revelstoke (B.C.)	0.060	6.5	3.9
Cree Lake (Sask.)	0.036	4.4	2.0
Wynyard (Sask.)	0.001	8.2	5.7
The Pas (Man.)	0.003	7.1	3.6
Bissett (Man.)	0.046	7.6	4.1
Moosonee (Ont.)	0.073	11.6	5.6
Simcoe (Ont.)	0.804	52.5	35.0
Maniwalki (Que.)	0.515	32.2	20.3
Quebec City (Que.)	0.573	57.2	25.8
Truro (N.S.)	0.432	30.0	10.9

* From Lau (1985).

Table 4. Modelled dry and dry/wet sulphate deposition ratios for Alberta sites (1982).[a]

Location	Dry Deposition ($kg\ ha^{-1}\ y^{-1}$)	Dry-Wet Ratio
Beaverlodge (Alta.)	4.8	0.94
Calgary	20.7	1.86
Coronation	18.6	2.16
Edmonton	21.0	1.94
Edson	18.6	1.94
Fort McMurray	21.0	3.18
Lethbridge	13.8	1.86
Red Deer	12.3	1.84
Rocky Mtn. House	20.2	1.94
Suffield	7.2	1.85
Whitecourt	21.9	1.43
Average	16.4	1.86[b]

[a] From Kociuba (1984)

[b] The average dry-wet ratio is determined by finding the ratio of the average dry (16.4 $kg\ ha^{-1}\ y^{-1}$) and average wet (8.8 $kg\ ha^{-1}\ y^{-1}$) depositions.

outputs of dry deposition, at this time there is a regrettable lack of sufficient data on: (a) continuously monitored SO_2, and (b) qualitative and quantitative characteristics of fine particulate aerosols. Almost all of the SO_2 monitoring in Alberta is point source oriented in response to regulation.

1.5 INTRODUCTION TO ATMOSPHERIC CHEMISTRY AND ACIDIC DEPOSITION PROCESSES: LITERATURE CITED

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2. EFFECTS OF ACIDIC DEPOSITION ON FORESTS

2.1 INTRODUCTION

Sulphur and nitrogen, the two most important components with respect to acidic deposition, are essential nutrients for plant growth. Sulphur deficiencies are widespread in regions such as the US Great Plains and adjacent Canadian Prairies (Brady 1984). Nitrogen deficiencies have also been postulated for forest soils as a result of leaching and uptake losses exceeding fixation (Smith 1981). Therefore, both elements combine fertilizing properties and acid forming capabilities and as a result, have been the focus of a great deal of research.

Carbon, principally in the form of carbon dioxide, is also essential for plant growth since it stimulates photosynthetic activity. Atmospheric concentrations of carbon dioxide have been increasing as a result of fossil fuel combustion, and other industrial sources, at a rate of about 3% per decade (Smith 1981). Between 1958 and 1978, the global concentration of carbon dioxide increased from 315 to 335 ppm as a direct result of anthropogenic activities (Oeschger et al. 1980). It has been estimated that in pre-industrial times the concentration may have been as low as 265 ppm (Bolin 1983). These trends have led to concerns over resultant atmospheric warming or the "greenhouse effect" with potential negative consequences for the biosphere (Bach et al. 1980).

Atmospheric carbon dioxide can also form carbonic acid during transformation processes. Because it is a weak acid, carbonic acid represents potential acidity and can act as a buffer. This is in direct contrast to strong acids such as nitric and sulphuric which dissociate completely (Krug and Frink 1983).

Carbon, like sulphur and nitrogen, is a major stimulator of plant growth which can have both beneficial and detrimental effects on overall forest productivity. All three substances can be derived from acidic deposition.

A fourth substance, ozone, is also very important. While it is not not acidic or an acidifying compound, because of its known direct deleterious effects on plants, and its joint action with other pollutants including acidic deposition, it must be considered in the present context. Ozone has been found to have the following effects on forests:

1. It has been found to cause damage and reduced growth of Ponderosa pine in the San Bernardino Mountains of southern California (Coyne and Bingham 1977) and has been implicated in white pine emergence tip burn in West Virginia and Tennessee (Berry and Ripperton 1963; Berry and Hepting 1964).
2. In California, a direct relationship between carbon dioxide increases and increases in ozone concentration has been found (Coyne and Bingham 1977).
3. It has been speculated that increasing global concentrations of ozone may also have an effect on temperature similar to that predicted for carbon dioxide. For example, if the global concentration of ozone were to double, temperatures could rise by 1°C (Lacis et al. 1981).
4. Ozone has been shown to produce more than additive effects on vegetation in the presence of other air pollutants, including those associated with acid emissions (Ormrod 1982).

Examples of ozone concentrations reported in the literature are in the range of 666-784 $\mu g\ m^{-3}$ for California, 255-911 $\mu g\ m^{-3}$ for Ohio, and as high as 788 $\mu g\ m^{-3}$ in the Black Forest of West Germany (McLaughlin 1985). Ozone has been implicated as a possible contributor to forest decline (see definition below) in both Europe and the eastern United States (Blank 1985).

2.2 FOREST CONCERNS RELATED TO ACIDIC DEPOSITION

Acidic deposition, whether wet or dry, has been documented as occurring in many areas of the world (McLaughlin 1985). For the purposes of definition, acidic precipitation is any wet event with a pH lower than 5.6, which is the pH of atmospheric waters in equilibrium with carbon dioxide (Krug and Frink 1983). Postel (1984b) has reported that in many heavily industrialized areas, precipitation may have acidity levels ten to thirty times greater than those which would be expected from an atmosphere free of pollution. However, because of the presence of undissociated acids in such precipitation, these values undoubtedly represent an overestimation of true acidity (Krug and Frink 1983). In spite of this, acidic rainfall (pH range 4 to 4.6) does occur over much of Europe and North America (Postel 1984b; Brady 1984).

The possible and potential effects of acidic deposition on forests are discussed in the following sections.

2.2.1 Forest Decline Phenomenon

There are three categories of plant diseases as defined by Manion (1981): biotic, abiotic, and decline. Of these disease types, decline is the hardest to define clearly. Manion, in an attempt at its definition, stated that declines "...result not from a single casual agent but from an interacting set of factors". McLaughlin (1985) further stated that declines are complex diseases resulting in a progressive weakening of trees leading to dieback, and the death of portions of the foliar canopy. Gradual loss of vigour involving a reduced growth rate and increased susceptibility to secondary biotic and abiotic stress typically ensues. Declines generally affect mature trees and ultimately death may occur unless the stress is removed or its effect controlled.

Forests with tree decline typically exhibit a wide and random variety of symptoms of biotic and abiotic stress (Woodman 1987). Because of the random symptom distribution patterns displayed in forests undergoing decline, it is almost impossible to define its exact causes (Hyink and Zedacker 1987).

Many forests in North America and Europe appear to be undergoing change that includes reduced productivity, dieback, and death. Reviews of these phenomena have been provided by Abrahamsen et al. (1976), Binns (1984), Morrison (1984), Postel (1984a,b,c, d,e,f, 1985), and McLaughlin (1985). Stand dynamics and the evaluation of the meaning of forest decline have been reviewed by Hyink and Zedacker (1987).

Acidic deposition has been implicated as a possible cause for the decline of forests in Norway (Overrein et al. 1980) and central Europe (Paces 1985; Van Breeman 1985). The decline of West German forests has been documented by Postel (1984a) who stated that 76% of the fir, 41% of the spruce, and 43% of the pine in the country were showing symptoms of stress. In total, the apparently stressed timber amounts to approximately 66% of West German forests. Similar results were documented by McLaughlin

(1985) and by Binns and Redfern (1983) in other locations throughout the world. In each of these cases, acidic deposition was suggested as the most probable cause of forest decline at the scales noted. In the United States, while a substantial lowering of forest productivity was very evident, no consensus or compelling documentation as to its causes were evident (refer to Linthurst 1984). A summary of possible effects of acidic deposition on soils, plants, and forests is provided in Table 5 along with the references relevant to these studies.

2.3 DIRECT EFFECTS OF ACIDIC DEPOSITION ON FORESTS

Abundant documentation exists, as shown in Tables 6 and 7, that acid precursors such as SO_2 can cause stomatal closure, affect water relations, reduce photosynthesis, and change carbon allocation. These effects can be mediated through modifications of phosphorylation, chlorophyll concentration, carboxylation, hormonal balance, and membrane integrity. Frank (1985), and Frank and Frank (1985), have also demonstrated that tree foliar pigments can be destroyed, producing symptoms very similar to those of the German forest decline, by exposure to chloroethanes. Chloroethanes and other halogenated chlorocarbons are also associated with acid emission sources and thus, are considered part of the acidic deposition problem.

Under some conditions, low level exposure of trees to sulphur and nitrogen oxides can, however, stimulate growth by fertilization. Similarly, many of these acid precursor pollutants can interact with elevated carbon dioxide, producing either a less deleterious or even stimulatory effect on forest vigour. As Legge et al. (1986) have pointed out, the supposed direct effects of the deposition of acidifying pollutants on biochemical processes in trees as shown in Tables 8 and 9 may, in fact, be indirect effects caused by the acidification of soils. If this is the case, one can understand the difficulty for silviculturalists in documenting either the definitive cause of symptoms or the dose response of vegetation to dry and wet acidic deposition.

2.4 INDIRECT EFFECTS OF ACIDIC DEPOSITION ON FORESTS

There are many indirect effects on forests attributed to acidic deposition. These include: canopy-pollutant interactions, soil acidification, nutrient leaching, weathering, and effects on microbial activity. Only canopy-pollutant interactions will be discussed here since the other topics are discussed at length in other parts of this synthesis.

2.4.1 Canopy-Pollutant Interactions

Forest canopies act as interceptors of both wet and dry deposition and in the process, alter the incident chemistry prior to contact with soils. Smith (1981) estimated that a one hectare model forest was capable of removing the following amounts of pollutants ($t\ y^{-1}$): O_3 - 9.6×10^4; SO_2 - 748; CO - 2.2; NOx - 0.38; and PAN - 0.17. Binns (1984) reported that up to 40% of precipitation intercepted by the forest canopy can re-evaporate along with its captured pollutants. This means that these materials may not pass through to other components of the ecosystem, at least at that location. Studies of deposition in Sweden on conifers by Granat (1983) showed that sulphur

Table 5. References to various effects of acidic deposition on soils, plants, forests, and ecosystems.

Effects as: Direct or Indirect	Effect	Reference
Direct Effects	Stomatal or mesophyll resistance	Black (1982)
	Photosynthesis	Carlson and Bazzaz (1982)
	Metabolism	Heath (1980)
	Hormones	Reid (1985)
	Membranes	Skärby and Sellden (1984)
	Growth	Higginbotham et al. (1985)
Indirect Effects	Canopy leaching	Foster and Morrison (1976)
	Soil Acidification:	
	-nutrient leaching	Morrison (1983)
	-aluminum and manganese	Ulrich et al. (1980)
	-phosphorus	Cook (1983)
	-weathering	Johnson et al. (1982b)
	-decomposition	Coleman (1983)
	-mycorrhizae	Patten (1983)
	-nitrogen fixation/ nitrification	Belser (1979)
	Fertilizer effects:	
	-sulphur	Smith (1981)
	-ammonium	Nihlgard (1985)
	Harvest technique	Johnson and Richter (1983)
	Forest reproduction	Cox (1983)
	Land use change and/ or succession	Krug and Frink (1983)

Table 6. The effects of pollutants on stomatal diffusive resistance and water status.

Species	Pollutant	Concentration	Comparison of relative diffusive resistance, treatment control [1]	Water status	Reference
Vicia faba	SO_2	0.25 - 1.0 ppm	Treated < Control	-	Majernik & Mansfield (1970)
Radish, cucumber, soybean	SO_2	0.15 ppm	Treated < Control	-	Beckerson & Hofstra (1979)
Radish, cucumber, soybean	O_3	0.15 ppm	Treated > Control	-	Beckerson & Hofstra (1979)
Radish, cucumber, soybean	$SO_2 + O_3$	0.15 ppm each	Treated >> Control	-	Beckerson & Hofstra (1979)
Phaseolus vulgaris	SO_2	520 $\mu g\ m^{-3}$	Treated > Control [2]	-	Bytnerowicz & Taylor (1983)
Phaseolus vulgaris	$SO_2 + O_3$	520 $\mu g\ m^{-3}$ + 390 $\mu g\ m^{-3}$	Treated >> Control [2]	-	Bytnerowicz & Taylor (1983)
Hybrid poplar	SO_2	0.25 ppm	Treated < Control (5-10%)	Older leaves, lower water potential	Biggs & Davis (1982)
Hybrid poplar	SO_2	0.12 ppm	No Difference	Older leaves, lower water potential	Biggs & Davis (1982)
Ulmus americana	SO_2	1.0 ppm	Treated < Control	-	Noland & Kozlowski (1979)
Ulmus americana	SO_2	2.0 ppm	Treated > Control	-	Noland & Kozlowski (1979)
Pinus picea, P. nigricans, P. sylvestris	SO_2		Treated > Control	-	Caput et al. (1978)

continued...

Table 6 (Concluded).

Species	Pollutant	Concentration	Comparison of relative diffusive resistance, treatment control [1]	Water status	Reference
Ginko biloba	SO_2	2.0 ppm	Treated < Control	-	Noland & Kozlowski (1979)
Pinus sylvestris	SO_2		Treated > Control	-	Farrar et al. (1977)
C_3 and C_4 Successional Species [3]	CO_2 SO_2	300, 600, 1200 ppm 0.25 ppm	Treated > Control No effect of SO_2	-	Carlson (1982)
Pinus contorta [4]	CO_2	1000 and 2000 ppm	No effect on R_L minimum	Minimum xylem pressure potential; no effect	Higginbotham et al. (1985)
Pinus contorta x P. banksiana	S-Gas	Concentration gradient downwind from sour gas plant	Generally higher adjacent to the gas plant	No measurable difference	Mayo et al. (1986) Legge et al. (1981)

[1] Relative diffusive resistance either as resistance measured, conductance, or inferred from transpiration.
[2] Returned to control values after fumigation.
[3] C_3 Chenopodium, Datura, Polygonum; C_4 Amaranthus and Setaria.
[4] Long term growth experiment seedlings grown 5 months at elevated CO_2.

Table 7. The effects of pollutants on photosynthesis and carbon allocation (1).

Species	Pollutant	Concentration	Effect on Photosynthesis (Ps)	C-allocation	Other effects	Reference
Wheat & Barley	Nitrogen	Increasing	Linear increase in photosynthesis with nitrogen regardless of the source	Ca affects translocation	K^+ deficiency reduces Ps	Natr (1975)
Lichens; Cladonia	SO_2	0.75-75.0 ppm	5% to 100% reduction in photosynthesis		Large K^+ leakage	Nieboer et al. (1976)
Pinus ponderosa	O_3	0.15 ppm (30 d) 0.30 ppm (30 d) 0.45 ppm (30 d)	Reduced Ps 10% Reduced Ps 70% Reduced Ps 85%	Lower needle polysaccharide level	Increased ascorbic acid content of needles	Miller et al. (1969)
Pinus contorta	CO_2 CO_2 CO_2	300 µL L^{-1} 1000 µL L^{-1} 2000 µL L^{-1}	6.2 mg dm^{-2} h^{-1} Net Ps 12.3 mg dm^{-2} h^{-1} Net Ps 8.9 mg dm^{-2} h^{-1} Net Ps	Maximum growth at 1000 ppm mostly as root growth		Higginbotham et al. (1985)
Alfalfa, bean, grass	O_3, NOx SO_2, PAN	Various - review	Reduced photosynthesis 0.5 ppm $\geq$ 1 h		Interaction with membranes, loss of Ca from cell wall	Heath (1980)
C_3 and C_4 (2) successional herbs	SO_2 and CO_2	300, 600, 1200 ppm CO_2; 0.0 or 0.25 ppm SO_2	SO_2 caused a slight reduction in Ps of C_3's and greater reduction in C_4's	SO_2 decreased growth in all but C_3 at 300 ppm		Carlson & Bazzaz (1982)

continued...

Table 7 (Continued).

Species	Pollutant	Concentration	Effect on Photosynthesis (Ps)	C-allocation	Other effects	Reference
Pinus ponderosa	Oxidant fumigations; O_3 San Bernardino Mts.	3 injury classes: I-Slight, II-Moderate, III-Severe Concentration implied from injury class: I-slight; II-moderate; III-severe	2 y needles class III lowest Ps; current needles, class I highest Ps; lowest = 1 mg CO_2 g^{-1} h^{-1} highest=12 mg CO_2 g^{-1} h^{-1}	CO_2 assimilation efficiency ratio highest in current class I	Current needles class II had very high conductances	Coyne & Bingham (1982)
Pinus strobus	Oxidant-ozone sensitive, intermediate and tolerant trees studied	125 to 339 h y^{-1} $\geq$ 0.08 ppm	Ps capacity of sensitive trees 4.5 mg CO_2 g^{-1} h^{-1} and resistant 4.6, i.e., no difference	Growth less in sensitive trees; less export of C to boles & roots in sensitive trees	Respiration higher in sensitive trees	McLaughlin et al. (1982)
Various - review	SO_2	Concentration that causes reduced photosynthesis varies with species;	Pea - .2 ppm causes 50% reduction; Vicia - .4 ppm causes 40% reduction; Atriplex - 1.4 ppm causes 15% reduction; Heteromeles - 1.8 ppm causes 50% reduction		ABA enhances inhibition of transpiration by SO_2 (2 ppm); high CO_2 results in less reduction of Ps by SO_2	Black (1982)
Pinus contorta x P. banksiana hybrid (?)	S-gas emissions, SO_2, H_2S, etc.	Gradient downwind from S-gas plant	Current foliage 2.8 mg g^{-1} h^{-1} at a distance; 2 y old needles 2.0 mg g^{-1} h^{-1} close to plant and 2.4 mg g^{-1} h^{-1} further from plant	Growth reduced by proximity to S source	Maximum leaf resistances highest close to S source	Legge et al. (1986)

continued...

Table 7 (Concluded).

Species	Pollutant	Concentration	Effect on Photosynthesis (Ps)	C-allocation	Other effects	Reference
Pinus strobus	SO_2	5 pphm for 2 h	Sensitive clones reduced Ps 27%; resistant clones 10%		No difference in needle length	Eckert & Houston 1980
Tomato (greenhouse)	NOx	2000 ppb	Low nutrient solution nitrogen 43 ppm results in + 3% yield of fruit; 170 ppm N in solution results in -13% yield; infers greater photosynthesis with low N		CO_2 + NOx gives greater yield than no CO_2 enrichment	Law & Mansfield 1982
Soybean	SO_2 + O_3 or acid rain	0.1 µl L^{-1}+ 0.5 µl L^{-1} or pH 3.4, 4.2, 5.0	Inhibited by SO_2 + O_3 but not by acid rain	Growth reduced by SO_2 + O_3 but not by acid rain	Nitrogen fixation reduced by SO_2 + O_3 but not by acid rain	Norby et al. (1985)
Liriodendron tulipifera Quercus alba Pinus virginiana	Acid rain	pH 5.7, 4.5, 4.0, 3.5	No reduction or enhancement	-	No effect on respiration	Kelly et al. (1984)

[1] Ps used to indicate some measure of photosynthesis, including infrared gas analysis, CO_2 incorporation, etc.
[2] C_3 plants include Chenopodium, Datura, Polygonum; C_4 plants Amaranthus and Setaria.
[3] Data from cut branches, therefore values are photosynthetic capacity.
[4] Data based upon Warburg manometric measurements - not comparable to infrared gas analysis or $^{14}CO_2$ methods.

Table 8. Biochemical effects of pollutants.

Species	Pollutant	Concentration	Lab=1 Field=2	Effect on Photosynthesis	Relation to Physiology, Growth, etc.	Reference
Pinus contorta x Pinus banksiana	SO_2	0-250 ppb 10-207 ppb	1 2	Linear reduction of ATP with increasing SO_2 - approx. 80% reduction at 225 ppb. Field foliage has 450 ng ATP g^{-1}. Lab cultured foliage 1460 ng ATP g^{-1}	Lab reduction of photosynthesis as ATP declined	Harvey and Legge (1979)
Pinus contorta	SO_2 aqueous		1	Chlorophyll destruction		Malhotra (1977)
Review	Ozone			Inhibition of nitrate reductase changes membrane permeability particularly K+ efflux	N metabolism	Tingey and Taylor (1982)
Dactylis glomerata Poa pratensis Lolium, Phleum	SO_2, NO_2 SO_2 + NO_2		1	Glutamate dehydrogenase increase with SO_2 (indicates ammonia assimilation) SO_2-no effect on nitrite reductase. NO_2-great increase nitrite reductase. SO_2 + NO_2-no increase nitrite reductase	SO_2-decreases photophosphorylation. SO_2 + NO_2-decreases photophosphorylation. NO_2-great increase in photophosphorylation.	Wellburn (1982)
Pinus ponderosa	O_3	0.30 ppm for 30 days	1	Higher ascorbic acid in injured needles. In one-year-old needles sugars reduced by O_3, polysaccharides decreased by 40%	Reduced sugars and polysaccharides related to reduced Ps and early needle drop.	Miller et al. (1969)

continued...

Table 8 (Concluded).

Species	Pollutant	Concentration	Lab=1 Field=2	Effect on Photosynthesis	Relation to Physiology, Growth, etc.	Reference
Various - review	SO_2	various	1	SO_2 enhances ABA induced stomatal closure- 2 ppm SO_2 on radish degrades chlorophyll - chloroplasts and mitochondria swell. Rubisco and PEP carboxylase competitively inhibited by SO_2, sulphite and bisulphite.	Membrane integrity organelle ultra-structure effect on stomata and various processes reduce photosynthesis.	Black (1982)
Review	Ozone, SO_2	various		O_3 at 0.05 $\mu L\ L^{-1}$ & SO_2 at 0.3 $\mu L\ L^{-1}$ can stimulate ethylene production (acid ppt) 50 ppb to 200 ppm for 1 h threshold	Ethylene causes a wide variety of responses- slow cell division, leaf & flower senescence, resin formation in pine, slow leaf expansion.	Reid (1985)
Picea omorica	Chloroethenes	tree exposed to trichloroethenes	2	Chlorophyll destruction	Developed symptoms of German dieback	Frank & Frank (1985)
Picea abies	Tri- or Tetra- chloroethene	14 $\mu g\ m^{-3}$ for 5 h	1	HPLC[1] of pigments very similar to that of naturally affected needles.		Frank (1985)

[1] HPLC = High Pressure Liquid Chromatography

Table 9. Effect of pollutants on reproductive biology.

Species	Location	Pollutant	Response	Condition	Conclusion	Reference
White pine		high pollution (SO_2?)	55 seeds/cone. Avg. seed wt 1.532 g. Pollen germination 60%	Area with high pollution	Areas with high pollution had fewer seeds/cone, lower average seed weight, lower % pollen germination	Houston & Dochinger (1977)
		low pollution	67 seeds/cone. Avg. seed wt 1.850 g. Pollen germination 83%	Area with low pollution		
Red pine		high pollution (SO_2?)	Avg. cone length, 44 mm Avg. seed wt 0.666 g Filled seed 50% Seed germin. 50% Pollen germin. 65% Avg. pollen tube length 92 mm	Area with high pollution	Areas with high pollution had fewer seeds/cone, lower avg. seed weight, lower % pollen germ.	Houston & Dochinger (1977)
		low pollution	Avg. cone length 47 mm Avg. seed wt .805 g Filled seed 68% Seed germ. 66% Pollen germ. 84% Avg. pollen tube length 113 mm	Area with low pollution		
Scots pine	Russia	SO_2	Avg. seed wt 4.85-5.75 g Cone length 32.1-35.6 mm Cone wt 2.39-3.03 g Avg. seed wt 5.47-6.67 g Cone length 39.5-42.4 mm Cone wt 3.81-5.91 g	Near copper smelter Clean (low SO_2)	Near copper smelter (high SO_2), lower cone length, cone weight, and avg. seed weight	Smith (1981)
Ponderosa pine		O_3	Reduced cone size			Miller (1973)
Ponderosa pine	British Columbia	SO_2	Reduced cone size	Near copper smelter		Scheffer & Hedgecock (1955)

continued...

Table 9 (Continued).

Species	Location	Pollutant	Response	Condition	Conclusion	Reference
Douglas fir	Oregon	"acid rain" pH 3 to 5.6	Seed emergence stimulated	Field conditions ambient rain excluded	Stimulation of Doug. fir emergence and growth emergence of hickory, maple, white pine, cedar, & birch	Lee & Weber (1979)
Sumac	Oregon	"acid rain" pH 3 to 5.6	Seed emergence inhibited			
Dogwood, Black birch, Yellow birch, Sugar maple	NewYork	pH 5-2.6 "rain"	Reduced pollen germination below pH 4.2	Lab study	Acid rain may affect reproductive processes	Van Ryne & Jacobson (1984) Van Ryne et al.(1986)
Oenothera	Canada	pH 5.6-2.6	pH $\leq$3.6 inhibited pollen germination and tube growth. Reduced stigmatic receptivity	Field plants		Cox (1984)
White pine	New York	pH 5.6,4.0,3.0	Stimulated seed germination. Inhibited seed germination at pH 4	Greenhouse	Response varies from stimulation to inhibition of seed germination	Raynal et al. (1982)
Acer rubrum			No effect			
Betula lutea			No effect			
Acer saccharum						
Tsuga canadensis						
Ponderosa pine	Oregon	O_3	Seedling emergence stimulated			Wilhour & Neely (1977)
Lepidium virginicum	-	SO_2	Reduced pollen germination 50% but not seed set		.6 ppm SO_2	DuBay and Murdy (1983)

continued...

Table 9 (Concluded).

Species	Location	Pollutant	Response	Condition	Conclusion	Reference
	Ontario.	"acid rain"	50% inhibition in pollen growth		Conifers most resistant, deciduous trees intermediate	Cox (1983)
Acer saccharum		3.9				
Populus tremuloides		3.7				
Betula papyrifera		3.6				
Pinus strobus		3.6				
P. banksiana		3.2				
Tsuga canadensis		2.95				

compounds were deposited in wet form in greater amounts than dry. Yearly average deposition rates were 0.90 and 0.32 g m^{-2} for wet and dry, respectively. In contrast, Höfken (1983) found that dry deposition exceeded wet deposition in a spruce forest and the rates varied by season. For example, he observed that the rates for dry sulphate deposition were 1400 and 2600 mg m^{-2} $month^{-1}$ for summer and winter, respectively. Corresponding seasonal rates for wet deposition were 300 and 600 mg m^{-2} $month^{-1}$.

Results obtained by Hofken (1983) for nitrogen compounds in wet and dry deposition were similar to those for sulphur. These data indicate that considerable amounts of both wet and dry deposition, particularly acidic ions, can be intercepted by leaves and stems and can undergo reactions with these vegetation parts and later be washed from the plant to undergo further interaction at the soil interface.

Throughfall may be defined as that portion of precipitation intercepted by the canopy but subsequently transferred to the soil below. The effects of this interception vary with the type of forest, i.e., hardwood versus softwood, as well as by species of tree involved. In general, hardwood canopies tend to raise the pH of the throughfall (Abrahamsen et al. 1976; Hoffman et al. 1980; Miller 1983; and Mollitor and Raynal 1983), while coniferous or softwood forests generally tend to lower pH. However, Miller (1983) reported that young Scots pine stands and Sitka spruce both appear to raise, rather than lower, pH.

Hoffman et al. (1980) reported that total acidity of throughfall was approximately the same as incident precipitation but that weak acids increased by 20-40% in the throughfall while strong acids decreased by similar amounts. This finding suggests that weak acids were exchanged for strong acids.

While hardwood canopies tend to decrease the H^+ concentration in the throughfall (Mollitor and Raynal 1983), total cation concentrations increase (Eaton et al. 1973) probably as a result of H^+ to cation exchange occurring in the canopy through contact between leaves and the precipitation. Eaton et al. (1973) found in their study that the concentration of sulphate also increased, thus providing a mobile anion to balance leaching cations. In comparison, concentrations of both nitrate and ammonium were lower in the throughfall than in incident precipitation, which suggested differential absorption (Eaton et al. 1973).

In general, conifers have been found to cause H^+ and cation concentrations to increase in throughfall. Again, this trend can be species specific as shown by Cole and Johnson (1977) and Binns (1984) in studies with Sitka spruce and Douglas fir respectively. Throughfall from these species is characterized by decreases in H^+ and increases in the concentration of SO_4^{2-}, K^+, Ca^{2+}, and Mg^{2+} in comparison with values found in the precipitation (Eaton et al. 1973). The studies of Miller (1983) on Scots pine indicated that this effect could also be age specific, with older trees of this species causing an increase in throughfall H^+, while H^+ decreased in the throughfall of young trees.

Stemflow refers to that portion of the intercepted precipitation that is carried down the stems, branches, and trunks of trees to the ground. In most cases stemflow in Scots pine, Sitka spruce, Japanese larch, birch (Miller 1983), lodgepole pine, and white spruce (Baker et al. 1977) was more acidic than throughfall. In all cases cited, stemflow had a lower pH than incident precipitation and decreased even when canopy effects on throughfall indicated a rise in pH.

The possibilities for indirect effects of acidic deposition on forests are almost limitless. From the moment that acidic materials come in contact with the canopy, various effects are possible. The canopy itself can exchange and modify precipitation in a number of ways, so that whatever reaches the ground may be different in its pH, molecular species of the acids, ionic content, and concentration in comparison with the incident precipitation. Upon entering the soil, precipitation is subjected to what is, in effect, a large, variable, and reactive exchange column. The soil can be acidified with increases in Al^{3+}, Mn^{2+}, or Fe^{3+} to toxic levels. Cations may be leached and microbial processes altered. The whole nitrogen budget may also be altered. Nodule formation may be inhibited, nitrogen fixation altered, and nitrification inhibited. The size and proportions of the nitrate-ammonium pools may also change and mycorrhizal relations may be altered. These possibilities are site-, species-, and situation-specific and each situation, therefore, is different and requires investigation prior to formulating opinions on possible effects and/or impacts that result from acidic deposition. There is little doubt that these kinds of effects can occur; what is in doubt is their importance to overall forest health and under what specific conditions they occur. For example, although NOx and its family of compounds are often cited as affecting vegetation as a result of acidic deposition, Vitousek et al. (1979) found that trenching and cutting alone were sufficient to cause nitrate losses from the soils of 19 different forests. Presumably, the loss or leaching of the mobile anion nitrate was balanced by an equivalent loss of cations to maintain the system in equilibrium. Thus, disturbance activities in forest ecosystems tend to mimic the results of acidic deposition.

2.5 INTERACTIVE EFFECTS OF ACIDIC DEPOSITION ON FORESTS

2.5.1 Interactive Effects on Forest Nutrition and Growth

Along with the direct effects of acidic deposition, a wide array of indirect effects are also possible. Such effects result from forest harvest practices, fertilization, and nutrient cycling, as they interact with acidic deposition.

Abrahamsen (1980) has reviewed the potential relationships between acidic deposition and plant nutrition. Using Mikaelis-Menton kinetic theory, he has pointed out that most forests are limited by the availability of nitrogen and that an overabundance of other nutrients cannot compensate for the deficiency of one element or limitation to growth. Therefore, in such a case, adding excess sulphur will not promote growth even though it is a plant nutrient. Instead, it may cause additional problems; fertilization with one element may cause deficiencies in others. For example, the additions of NH_4^+ to European forests as a result of acidic deposition may be the cause of much of the observed forest dieback or decline (Nihlgard 1985). Discussions of nutrient cycling and supply with respect to forest management practices may be found in the reviews of Khanna and Ulrich (1984), Miller (1984), and Gosz (1984). In spite of this body of knowledge, considerable disagreement still exists over the exact causes of forest decline. For example, Tabatabai (1985) feels that pH changes that result from acidic deposition are minimized by the natural buffering capacity of soils and that the resulting additions of N and S will be beneficial. It appears from his discussion that near pollution sources, deposition may cause adverse effects on crops through the

acidifying process, but at long distances from sources, deposition does not appear to be a concern. Mayo (1987), in his review, documents some of the major investigations that show beneficial, detrimental, or no effects on vegetation as a result of acidic deposition. Many of the studies which have shown either beneficial or no effects of acidic deposition dealt with cereal crops in fumigation experiments carried out in greenhouses with artificial acidic rain. As Tabatabai (1985) stated in his review, experiments with simulated acidic rain will not provide the information needed to clearly define effects on a ambient deposition dose-response basis. Many of the studies that showed detrimental effects as a result of exposure to gaseous pollutants were conducted in the field and all dealt with trees of commercial interest. The results of these latter studies clearly showed that second and third order effects were often found in the trees. It may be that this degree of interaction was not tested in the studies cited as showing benign effects of acidic deposition on vegetation. It is also possible that the artificial "acidic rain" concocted for use in experiments may have led to simplistic and unrealistic results, in terms of the real world. Such studies are, however, of value as long as they are then proven under ambient conditions in the field with the same results. An example of such an experimental approach may be found in the studies of Legge et al. (1976) with sulphur dioxide, where laboratory fumigation studies were repeated in the field close to a sulphur gas emitting source and both lab and field experiments produced similar results.

2.5.2 Timber Harvesting and Acidic Deposition

Forest management practices have been found to affect nutrient cycling (see for example Vitousek et al. 1979). Variables of concern include the type of harvest, such as whole tree or bole only, and length of rotation between cuts. For example, an 80-year rotation with only saw log removal will produce very different results with respect to nutrient losses than will whole-tree harvest biomass systems of management.

Johnson and Richter (1984) have reviewed the effects of harvesting and pollution on several forest ecosystems in the United States and West Germany. They reported that clearcutting operations increased the leaching of both nitrate and calcium. They also reported that whole tree harvesting results in significantly higher losses of N, S, Ca, K, and Mg from the system than does bole harvesting. During their studies it was noted that sulphur input in areas subject to acidic deposition was higher than removal rates by leaching but that this was not so for nitrogen (Johnson et al. 1982a; Johnson and Richter 1984). They also concluded that both harvesting and acidic deposition can result in base cation loss and that, of the two processes, harvesting was likely to be the most detrimental. These studies reaffirm the conclusions put forth by Tabatabai (1985) that the nutrient in shortest supply dictates the form of the effects on the system. In the aforementioned studies, nitrogen was found to be the limiting factor. Forest management practices would likely be more detrimental if acidic deposition did not occur because of the losses of nitrogen due to methods such as clear cutting. These nitrogen losses are to some extent ameliorated by nitrogen deposition in the form of acidic precipitation and dry deposition.

2.5.3 Effects of Acidic Deposition on Tree Reproduction

A summary of the effects of acidic deposition on the reproductive processes of trees is shown in Table 9 (Mayo 1987). Generally, pollutants reduce pollen germination and tube growth and there is considerable evidence that cone size, weight, and numbers of seeds/cone are also reduced (Scheffer and Hedgecock 1955; Cox 1983, 1984; DuBay and Murdy 1983; and Van Ryne and Jacobson 1984). The results of investigations into effects on seed germination are contradictory. For example, Bonte (1982) and Raynal et al. (1982) found that acidic precipitation and high pollutant levels inhibited germination in red pine and red maple, respectively, while Lee and Webber (1979) and Raynal et al. (1982) found a stimulatory effect for fir and white pine. Seedling emergence studies seem to indicate inhibition by acidic precipitation for most species while ozone appears to stimulate emergence at least for Ponderosa pine (Wilhour and Neely 1977). From the literature it appears that pollutants such as SO_2, ozone, and acidic precipitation can affect reproduction; however, these effects are quite varied and are distinctly species and site specific.

2.6 EFFECTS OF ACIDIC DEPOSITION ON PLANT COMMUNITIES

Few studies were reviewed that focused on whole forest effects and responses to acidic deposition. Very few forest plant community studies have been completed. However, population studies and ecotype investigations have been completed and the changes in reproductive biology described in the previous section would suggest that varied responses leading to community changes may result from acidic deposition. Law and Mansfield (1982), in studies on NOx, concluded that varietal resistance to nitrogen uptake may cause variable uptake rates. Studies by Garsed and Rutter (1982) showed wide differences in sensitivity to SO_2 among three different species of pine. Their studies suggested that pollution could exert a strong selective pressure both within and between species. Chronic pollution has also been shown to cause simplification of community structure (McClenahen 1978). All of these studies suggest that chronic low level pollution could affect forest community diversity and perhaps even dominance structure. Pielou (1982), however, when testing the species composition along potential pollutant gradients adjacent to an Oil Sands plant in Alberta, found no evidence of compositional changes.

It has already been mentioned that there are those who feel that secondary succession is an acidifying process and that changing land use involving succession back to coniferous growth may be a major cause of soil acidification (Rosenqvist 1978; Overrein et al. 1980; and Krug and Frink 1983). Therefore, rather than acidic deposition altering succession, succession may be the cause of soil acidification in some instances.

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3. ACIDIC DEPOSITION EFFECTS ON AGRICULTURE

Agriculture and grazing are dominant in four ecoregions of Alberta: Short Grass, Mixed Grass, Fescue Grass, and Aspen Parkland Regions, which cover about 25% of Alberta (Strong and Leggat 1981). Thus, the effect of air pollutants on agriculture is of both economic and ecological concern.

Agricultural production contributed 10.2% of Alberta's gross domestic product in 1981, with grain crops such as wheat and barley accounting for over 75% of Alberta's total farm cash receipts (Alberta Agriculture Statistics Branch, letter 1985). Almost 30% of Alberta's land area is used for farming, with 12% being cultivated at a given time (Alberta Agriculture 1982). Approximately half (nearly 6 million hectares) of Alberta's 12.5 million hectares of improved land is utilized for grain crops, including barley (2.6 million hectares), wheat (2.7 million hectares), rye (.12 million hectares), and mixed grains (.06 million hectares). Forages, including grasses and leguminous forages, are farmed on approximately 1.8 million hectares. Oil-seed crops occupy .6 hectares. Other important crops are sugar beets (16,200 hectares), potatoes (8,000 hectares), field beans (3,600 hectares), and field peas (3,600 hectares).

The following discussion has been divided into three major sections. The first section deals with the effects of wet acidic deposition on agriculture; the second section discusses the effects of dry deposition; and the third section deals with the effects of various mixtures of acid forming gases and others on agriculture.

3.1 EFFECTS OF ACIDIC PRECIPITATION ON CROPS

The effects of acidic precipitation on agricultural plants include reduction in growth and yield, interference with reproduction, foliar injury, and alteration of foliar processes such as fertilization, buffering, leaching, and nutrient accumulation. For both ecological and economic concerns, plant growth, yield, and reproduction are the most important plant responses. In the experiments reviewed by Torn et al. (1987), dicotyledons appeared more likely to show inhibited growth than monocotyledons. None of the experiments reviewed by these authors showed growth inhibition at steady state simulated acidic rain with pH values above 4.0.

3.2 FOLIAR INJURY

Visible foliar injury (VFI), is the most frequently reported symptom of plant response to simulated acidic precipitation. However, a direct correlation between visible foliar injury and yield has yet to be established (Evans et al. 1981a, 1982c; Johnston et al. 1981; Lee 1981; and Proctor 1983), and there is no known index of VFI correlated with either growth or yield. Simulated acidic rain has, however, induced visible injury on the foliage, fruits, and flowers of agricultural and horticultural crop species. The literature on the topic indicates that no clearcut cause-effect relationships exist; for example, there are cases where injured plants exhibited stimulated growth, and others where growth was inhibited (Hindawi et al. 1980; Evans et al. 1981a).

Foliar injury may reduce productivity through structural changes such as inducing necrotic lesions or curling and wilting of the leaf, and/or through physiological changes such as altering diffusive resistance or reducing intercellular spaces. The

indirect and direct effects of foliar injury attributed to acidic deposition are summarized in Table 10 (Torn et al. 1987).

Most reports of VFI occur at or below pH 3.5. Sensitive species exposed to rain events of pH 3.0 lasting two or more hours face a significant risk of foliar injury. Current annual average pH of ambient rain in Western Canada is greater than 5 (U.S. National Research Council 1983, Lau and Das 1985) and, therefore, poses little risk to most field crops with respect to incurring VFI.

The preceding discussion, however, must be evaluated in the context of the characteristics of ambient precipitation. The chemical composition of rainfall is never constant. The chemistry of rain is known to vary within a given event (Pratt et al. 1983) and between events (Krupa et al. 1987). In addition, the frequency distributions of ion concentrations in precipitation are skewed to the left (low concentrations) with a long tail toward higher concentrations. These types of "non-normal" distributions provide overestimations of the mean values for ions. Thus, experiments with "simulated rain" with constant chemical composition derived from the mean of ambient precipitation composition should be viewed as highly artificial and inappropriate in the context of the real world situation.

The economic value of plants that sustain foliar or fruit damage can be greatly reduced primarily because of appearance. However, actual yield appears not to be affected by foliar injury for grains, forages, and processed fruits and vegetables.

Plants that exhibit injured leaf surfaces are likely to be more susceptible to pathogen attack. Lesions formed on leaves by either wet or dry deposition can provide infection sites for pathogens (Shriner and Cowling 1980). Evans and Curry (1979) observed that in soybean, the vascular tissue induced depressions at the base of trichomes and stomata in which acidic droplets accumulated and lesions were formed. Penetration to the inner leaf structures by acidic solutions, possibly through micropores and/or glandular hairs, is likely enhanced around both trichomes and stomata (Crafts 1961).

At the cellular level, foliar injury induced by acidic rain has been shown to cause a reduction in mesophyll conductance, intercellular space, and the size of starch granules (Ferenbaugh 1976; Neufeld et al. 1985a). Consequently, nutrient uptake and carbohydrate storage may be affected, in turn affecting fruit set.

Wet acidic deposition affects leaf surface tissues initially, whereas dry deposition causes injury to internal cells (Evans et al. 1977; Evans and Curry 1979). As a result of acidic, wet deposition, external lesions may eventually lead to internal leaf cell injury (Evans et al. 1977; Hindawi et al. 1980). Necrotic lesions can also be formed where entire cell strata are dead and bleached cells of chlorotic lesions exhibit a reduced level of metabolism.

Acidic wet deposition has been found to form galls (elevated portions of leaves) in bush bean, sunflower, wormwood, wax bean, and spinach (Adams and Hutchinson 1984). Because of the shape of galls, once the initial injury is caused, further accumulations of acidic droplets are prevented; thus galls actually reduce further injury to the plant (Evans et al. 1977). The main effect of galls would likely be in reduced market value of leafy commercial products because of their negative visual appeal.

Morphological changes in leaf tissue in response to simulated acidic wet deposition, as noted, cause variations in the effects of a particular exposure to

Table 10. Potential effects of acidic precipitation on vegetation.

DIRECT EFFECTS

1. Damage to protective surface structures such as cuticle.
2. Interference with normal functioning of guard cells.
3. Poisoning of plant cells after diffusion of acidic substances through stomata or cuticle.
4. Disturbances of normal metabolism or growth processes without necrosis of plant cells.
5. Alteration of leaf- and root exudation processes.
6. Interference with reproductive processes.
7. Joint efforts with other environmental stress factors.

INDIRECT EFFECTS

1. Accelerated leaching of substances from foliar organs.
2. Increased susceptibility to drought and other environmental stress factors.
3. Alteration of symbiotic associations.
4. Alteration of host/parasite interactions.

Adapted from Morrison (1984) and Tamm and Cowling (1976)

simulated acidic rain. Galls act as protective mechanisms and lesions formed around stomatal openings also tend to protect the plant following a period of initial injury. Stomata tend to close in the presence of acids (Plocher et al. 1985). Other depressions formed as a result of acidic action on the leaf surface, for example, erosion of waxes or cell collapse, can increase water capacity and retention times, thereby increasing the probability of injury by increasing contact time with acids (Evans et al. 1977; Jacobson and Van Lueken 1977; and Evans and Curry 1979). In other experiments cited by the previous authors, acidic precipitation caused guard cells surrounding stomata to increase in turgor, resulting in a reduction in diffusive resistance to gas exchange. This effect may cause affected plants to be prone to water stress and wilting. Since lower diffusive résistance can also result in higher photosynthetic uptake, the net effect on plant response on productivity is not clear (Torn et al. 1987). Free hydrogen ions may also affect internal cellular functions through reduction in ATP activity if proton concentrations across membranes are changed. Exposure to acidic precipitation has also been shown to cause chlorophyll levels in plants to decrease (both chlorophyll a and b) (Ferenbaugh 1976; Hindawi et al. 1980; and Johnston et al. 1981).

The stage of plant development at the time of exposure to acidic deposition can influence the nature of the response and this also varies by species. Foliar injury is most pronounced on some species just prior to full leaf expansion (Evans 1984b). More commonly, newly expanded and older pre-senescent leaves are the most susceptible to acidic deposition and show the symptoms of VFI (Evans et al. 1977, 1981a; Evans and Curry 1979; Keever and Jacobson 1983a; and Neufeld et al. 1985a). The effects of VFI, however, are not clear. For example, in experiments with soybean exposed to simulated acidic precipitation, Evans et al. (1977) found that leaves were least sensitive prior to expansion but that newly expanded leaves were quite sensitive until 20 days old. Significantly, these experiments showed that no injury or VFI was apparent on these same plants at harvest, suggesting that the effect was not permanent or really detrimental to either the plant or to its marketability.

Rapidly expanding leaves have incomplete wax coverage, leaving portions of the cuticle exposed and, therefore, susceptible to acid injury (Neufeld et al. 1985b). The cuticular waxes may act as a barrier preventing aqueous ions from penetrating the leaf surface. The cuticle is also more hydrophilic than are the surface waxes; thus, expanding leaves have a higher wettability and water retention than do unexpanded or fully expanded leaves. In addition to these factors, shape of the emerging leaves can also contribute to their higher wettability and consequential susceptibility to acid effects (Neufeld et al. 1985b).

Wettability is a general term describing the amount of leaf surface area in contact with and retention of a water droplet and it is positively correlated with the degree of foliar injury but not necessarily with stress threshold (Keever and Jacobson 1983c). Susceptibility to foliar injury in relation to acidic deposition and the dosage level necessary to cause visual effects and natural plant resistance to foliar injury are not directly correlated or linked (Neufeld et al. 1985b). Threshold is defined as the dose (in terms of concentration of acid) that is sufficiently high that any higher dosage will result in a deleterious effect such as VFI. However, the concept of "a" single threshold is controversial and is subject to debate. Variability in plant

response to pollutant stress exists at the population, genus, species and cultivar levels. Further, plant response to a given pollutant is highly variable due to the influence of a number of time oriented parameters such as: the presence or absence of other pollutants, pathogens and pests; physical climatology; soil conditions and the dynamics of plant growth itself. Thus, is is more appropriate to consider a range or series of threshold values (Krupa and Kickert 1987).

Morphological leaf characteristics vary by species, cultivar, and stage of plant development. This variation in leaf shape may partially account for the differences in sensitivity to acid induced VFI found throughout the literature. Growth conditions affect the leaf surface and also affect plant sensitivity to acidic precipitation (Neufeld et al. 1985b). Agricultural plants in general have a lower resistance to foliar injury when grown in controlled environments compared with field grown varieties of the same species (Evans et al. 1981a, 1982b; Irving and Miller 1981; Cohen et al. 1982; Troiano et al. 1982; and Keever and Jacobson 1983b). This last point is extremely important when one considers that most of the experimental evidence indicating VFI as a result of acidic deposition was compiled using simulated acidic rain in controlled enviromental conditions.

An increase in acidity, frequency of occurrence, duration of exposure, and/or number of simulated acidic rain events increases the extent and degree of foliar injury (Evans and Curry 1979; Jacobson 1984). More frequent events allow less time for leaf recovery and may prevent the leaf from drying, which in turn allows pathogens more time to attack. The occurrence of injury is positively correlated with the length of time that the leaf is wet, and negatively correlated with the number of days between exposures (Irving 1983). By contrast, for gaseous pollutants or dry deposition, the occurrence of injury increases as the concentration and duration of the exposure increase.

Extreme variation in the pH of acidic rain also appears to be an important factor in production of foliar injury. Rain events with a varying pH giving a volume-rated mean pH of 3.0 will tend to induce more foliar injury than will the same number of events with rain at constant pH 3.0 (Irving and Miller 1981; Johnston et al. 1981; and Lefohn and Brocksen 1984). The reasons for these findings are not clear at this time.

3.3 SENSITIVITY OF PLANTS TO FOLIAR INJURY CAUSED BY WET ACIDIC DEPOSITION

Susceptibility to foliar injury from acidic deposition varies among species, and among cultivars within a species. The relative sensitivity of 36 crop species was analysed, based on data from 13 field and 14 controlled environment experiments where plants were exposed to simulated wet acidic deposition (Table 11). The highest pH resulting in VFI and the lowest pH applied without resulting in VFI for a variety of plants are shown in Table 11. The range between the two pH values approximates a threshold for foliar injury, for each cultivar tested, under the conditions when the experiments were conducted. Crops grown in a controlled environment consistently displayed a lower tolerance to acidic deposition than did field grown crops.

The dose at which 50% of the plants sustained significant VFI was pH 3.0. This corresponds well with thresholds of pH 3.0-3.5 estimated by other investigators (Torn et al. 1987). Simulated rain in the ambient mean pH range of 4.0 caused foliar injury in 9% of the experiments, only one of which was conducted under field conditions. Below

Table 11. Visible foliar injury resulting from simulated wet acidic deposition: pH threshold. (From Torn et al. 1987)

Species	Highest pH with Foliar Injury	Lowest pH with No Injury	Growth Conditions[1]	Reference
ROOT				
Beet cv. Detroit Dark Red	4.0	5.6	C.E.	1
Beet	4.0	-	F	2
Carrot cv. Danvers	3.0	3.5	C.E.	1
Radish	4.2	5.6	C.E.	3
Radish	2.7	-	F	4
Radish	2.8	-	F	5
Radish cv. Cherry Belle	3.5	4.0	C.E.	1
LEAFY				
Lettuce	3.1	4.0	C.E.	3
Lettuce, Bibb cv. Limestone	3.5	4.0	C.E.	1
Lettuce, head cv. Great Lakes	3.5	4.0	C.E.	1
Mustard green cv. Southern Giant	3.5	4.0	C.E.	1
Spinach cv. improved thick leaf	3.5	4.0	C.E.	1
Swiss chard cv. Lucullus	4.0	5.6	C.E.	1
Tobacco cv. Burley 21	3.5	4.0	C.E.	1
COLE				
Broccoli cv. Italian green	3.5	4.0	C.E.	1
Cabbage	3.0	3.5	C.E.	1
Cauliflower cv. Early Snowball	3.5	4.0	C.E.	1
TUBER				
Potato cv. White Rose	3.5	4.0	C.E.	1
LEGUME				
Alfalfa cv. Honeoye	3.1	4.0	C.E.	3
Alfalfa cv. Honeoye	-	2.7	F	5
Alfalfa cv. Vernal	3.5	4.0	C.E.	1
Bean, bush	2.5	3.0	C.E.	6
Bean, bush	3.0	-	C.E.	7
Bean, bush	3.2	4.0	C.E.	8
Bean, kidney	3.2	-	C.E.	9
Bean, kidney	-	2.8	C.E.	10
Bean, kidney	-	2.7	F	5
Bean, pinto	3.0	4.0	C.E.	11
Bean, snap	-	2.6	F	12
Greenpea cv. Marvel	3.5	4.0	C.E.	1
Peanut cv. Tennessee Red	3.5	4.0	C.E.	1
Red clover cv. Kenland	3.5	4.0	C.E.	1
Soybean	2.9	-	C.E.	13
Soybean cv. Evans (G-0)	3.5	4.0	C.E.	1
Soybean cv. Hark(G-1)	3.5	4.0	C.E.	1
Soybean cv. Norman	3.5	4.0	C.E.	1
Soybean cv. OR-10	4.0	5.6	C.E.	1
Soybean cv. Amsoy 71	3.3	4.1	F	14

continued...

Table 11. (Continued).

Species	Highest pH with Foliar Injury	Lowest pH with No Injury	Growth Conditions[1]	Reference
LEGUMES (continued)				
Soybean cv. Amsoy 71	2.7	3.1	F	15
Soybean cv. Davis	3.4	4.2	C.E.	16
Soybean cv. Davis	3.2	4.0	F	17
Soybean cv. Wells	-	3.0	C.E.	18
Soybean cv. Wells	-	2.8	F	19
Soybean cv. Wells	-	3.0	F	18
FRUIT				
Apple blossom, Golden Delicious	3.0	4.0	F	20
Apple blossom, McIntosh	3.5	-	F	21
Apple foliage		2.5	F	21
Apple foliage, Empire		2.5	F	21
Apple foliage, Golden Delicious	3.0	4.0	F	20
Apple foliage, Golden Delicious	-	2.5	F	21
Apple foliage, McIntosh	-	2.5	F	21
Cucumber cv. 5116 Cresta	3.5	4.0	C.E.	1
Grape leaves	2.5	-	F	22
Green pepper cv. Calif. Wonder	4.0	5.6	C.E.	1
Strawberry cv. Quinalt	3.0	3.5	C.E.	1
Tomato cv. Patio	3.5	4.0	C.E.	1
FLOWER				
Sunflower	3.2	-	C.E.	23
Zinnia flower petals	2.8	-	C.E.	24
Zinnia foliage	2.8	-	C.E.	24
GRAIN				
Barley cv. Steptoe	-	3.0	C.E.	1
Corn cv. Golden Midget	3.0	3.5	C.E.	1
Corn cv. Pioneer 3992	-	3.0	F	25
Oats cv. Cayuse	-	3.0	C.E.	1
Wheat	-	2.7	C.E.	3
Wheat cv. Fieldwin	-	3.0	C.E.	1
BULB				
Onion cv. Sweet Spanish	-	3.0	C.E.	1
FORAGE				
Bluegrass cv. Newport	4.0	5.6	C.E.	1
Fescue cv. Alta Tall	3.5	4.0	C.E.	1
Orchardgrass cv. Potomac	3.5	4.0	C.E.	1
Ryegrass cv. Linn	3.5	4.0	C.E.	1
Ryegrass, perennial	-	3.0	C.E.	
Timothy cv. Climax	3.5	4.0	C.E.	1

[1] C.E. = Controlled Environment
F = Field Grown
- = Information not available

continued...

Table 11. (Concluded).

References:
1. Lee et al. (1981)
2. Evans et al. (1982a)
3. Evans et al. (1982c)
4. Troiano et al. (1982)
5. Evans et al. (1982b)
6. Ferenbaugh (1976)
7. Hindawi et al. (1980)
8. Johnston et al. (1981)
9. Shriner (1974)
10. Paparozzi (1981)
11. Evans et al. (1980)
12. Troiano et al. (1984)
13. Evans and Curry (1979)
14. Evans et al. (1983)
15. Evans et al. (1981c)
16. Norby and Luxmoore (1983)
17. Brewer and Heagle (1983)
18. Irving and Miller (1981)
19. Troiano et al. (1983)
20. Proctor (1983)
21. Forsline et al. (1983b)
22. Forsline et al. (1983a)
23. Jacobson and Van Leuken (1977)
24. Keever and Jacobson (1983a)
25. Plocher et al. (1985)

pH 2.5, 70% of the cultivars showed foliar injury. As previously stated, it is important to note that in many of these experiments the use of "simulated rain" with constant chemical composition derived from the mean values of precipitation pH and chemical composition, should be considered as highly artificial and unrelated to ambient conditions.

The groups of crops most susceptible to visible injury were, from most to least susceptible, root, leafy, cole, legume, fruit, grain, and leafy and seed forage crops respectively. The potential for economic loss was greatest for leafy, cole, and fruit crops. Leafy crops showed slightly less vulnerability to acidity induced foliar injury than did root crops. The threat to the economics of yield is, however, greater with the leafy crops which may lose commercial value if blemished. The threshold for injury to cole foliage is pH 3.0 to 3.5 which is higher than for leafy crops. Sensitivity of legume species varied, with plants such as soybean tending to be most susceptible to simulated acidic rain, likely due to their higher wettability. Foliar injury was observed for almost all fruit species studied. In addition, perennial fruit trees have shown latent foliar injury after cessation of acidic rain treatments. However, growth of annual fruit crops is, in general, stimulated by simulated acidic rain. Monocots, such as wheat, barley, and timothy were found to be resistant to foliar injury when exposed to simulated acidic rain above pH 2.5 (Torn et al. 1987).

3.3.1 Direct Foliar Effects of Wet Acidic Deposition

The plant leaf is composed of permeable tissue with continuous exchange of gases, water, and dissolved substances. Foliage may react chemically with acidic solutions upon contact without sustaining any change in its physical structure. Foliar fertilization, buffering, and leaching are all processes that have been investigated in this regard with respect to the effects of acidic deposition on plants. The acidic solution may represent wet or dry deposition that has hydrolyzed on the leaf's surface. These types of processes can result in direct but subtle effects on a plant because they may be active on internal processes.

3.3.1.1 Foliar Fertilization. Acidic deposition can act as a source of the nutrients nitrogen and sulphur that become available to plants if absorbed by the leaf (Irving and Miller 1981; Troiano et al. 1983; and Evans 1984). This process, termed foliar fertilization, can be both beneficial and detrimental to plants. Direct application of nutrients in this manner is a fast way of supplying nutrients to leaves although transfer of the fertilizer away from the sites of entry is a slow process (Garcia and Hanway 1976). Nutrients applied to the foliage pose the risk of inducing foliar injury (Neumann et al. 1981). Although there are insufficient data for a definitive conclusion, it is widely assumed that little of the nutrients contained in ambient precipitation penetrate the foliage to any degree (Evans et al. 1981, 1983; Evans 1984b). Even commercially available foliar fertilizers, which use added surfactants to aid foliar penetration, have had limited success in stimulating plant growth (Torn et al. 1987). Reductions in yield often correlated with foliar injury from fertilizer salts are often cited to be the result of nutrient application at high concentrations. Neumann et al. (1981) concluded that all osmotically active fertilizer compounds can induce plasmolytic damage when at sufficiently high concentrations to penetrate the leaf. In fact, fertilizer doses small

enough to prevent foliar injury may not allow penetration of enough fertilizer to stimulate plant growth (Neumann et al. 1981).

In their research on acidic rain, Evans et al. (1983, 1984) and Irving and Miller (1981) have considered the effects of the nutrients being added in precipitation. Evans et al. (1983) applied simulated acidic rain at pH 2.7 to soybeans. The plants were thus exposed to 10 times the ambient atmospheric levels of N and S. The net effect of this treatment was a 23% reduction in seed yield. It would appear that any fertilization effect of the acidic deposition was not sufficient to offset the detrimental effects of acidity.

Because the concentration and total deposition of nitrogen and sulphur in acidic precipitation are far lower than those found in commercial foliar fertilizers, it appears unlikely that significant benefit to crops will be realized in the form of foliar fertilizer (Evans et al. 1981a). This is particularly true when one considers that even the commercial foliar fertilizers have had limited success in improving plant growth except at particular times and for short periods.

3.3.1.2 Foliar Buffering. Some plants appear to develop little or no foliar injury from acidic precipitation. It is possible that the plant tissue may effectively buffer the acid before any significant physical or physiological injury can occur, and this ability may differ among species (Craker and Bernstein 1984).

Craker and Bernstein (1984) investigated the buffering ability of red kidney bean, wheat, red clover, soybean, corn, and timothy by soaking leaf tissue in simulated acidic rain solutions (pH 2.0, 3.0, or 4.0). In each case the pH of the solution rose within four hours. Subsequent visual analysis of leaf tissue injury suggested that the leaves with greater buffering capacity were more susceptible to foliar injury. Adams and Hutchinson (1984) found that the ability of the leaf to buffer simulated acidic precipitation was directly correlated with the extent of injury sustained. Foliar leaching of potassium associated with exposure to simulated acidic rain may be a secondary effect of foliar injury and may account for part of the buffering capability (Keever and Jacobson 1983a). These results support the hypothesis that the buffering ability of leaves is due to the release of cellular materials from dead or disrupted cells. Senescent leaves have a much greater buffering capacity than young healthy leaves. Bicarbonate stored in cell walls for photosynthetic activity may act to neutralize acidic deposition (Oertli et al. 1977). This should also mean that leaf litter layers have a high capacity to counteract the effects of acidic deposition.

It is also possible that leachates or superficial aggregates of particulate matter contribute to the buffering of excess hydrogen. For example, foliar alkaline deposits formed from foliar leachates and atmospheric CO_2 can neutralize acidic solutions (Adams and Hutchinson 1984). In another investigation, surface contaminants and microflora were removed from leaves prior to treatment with acidic rain with no effect on the buffering ability of the leaves (Craker and Bernstein 1984).

3.3.1.3 Foliar Leaching. Foliar leaching has been studied by numerous investigators by examining the chemical constituents of leachate following leaf exposure to simulated acidic solutions (Evans et al. 1977; Hindawi et al. 1980; Keever and Jacobson 1983a,b,c;

and Adams and Hutchinson 1984). The results of these studies showed that leaching rates of Ca, K, and Mg for seven out of nine plant species tested increased after exposure to simulated acidic rain. Johnston et al. (1981), however, found both increased and decreased leaching of foliar K in soybean subjected to simulated acidic rain. In other studies on soybean conducted by Hindawi et al. (1980), no effect on the leaching of K was found but levels of both Ca and Mg increased, as did P and NO_3. In the previously cited work by Johnston et al. (1981), these ions were not measured. On the basis of these studies it would appear that simulated acidic precipitation does cause the leaching of cations from leaves. Some of the possible mechanisms are discussed below.

Foliar potassium was found to increase in concentration in the leachate of zinnias and soybean following exposure to acidic solutions (Keever and Jacobson 1983a,c). In the case of zinnia, no effect on leaching was found at pH 4.0 or at the control pH 5.6; however, at pH 2.8, K was found to increase in the leachate as measured by Rb86. This loss of K from plant leaves was further accelerated under nutrient rich conditions. An increase in leaching of foliar K associated with foliar injury was also found in soybean and bean at a threshold pH of 4.0 by Keever and Jacobson (1983c) and Evans et al. (1981), respectively. The threshold for leaching was of the same order of magnitude as that observed for foliar injury in soybean (Evans et al. 1983c; Keever and Jacobson 1983c). The foliar loss of potassium may have been due to the death and subsequent degradation of cells resulting from exposure to a low pH solution (Keever and Jacobson 1983c).

Foliar buffering and increases in leaching due to acidity are undoubtedly related processes. Buffering on the leaf surface is aided by alkaline deposits formed by atmospheric deposition or by exuded foliar salts. Leaching occurs as exchangeable cations in the cuticle and cell walls and these cations are exchanged for H^+ in acidic solutions (Adams and Hutchinson 1984). The cuticle forms a barrier for ion movement in and out of the tissue, and the cuticle waxes play a role in inhibiting leaching of foliar nutrients (Neufeld et al. 1985b). Cuticular micropores are the principal route for cation exchange and loss, as well as for entry of chemicals into the intercellular structures of leaves (Adams and Hutchinson 1984; Evans 1984). Greater wettability is correlated with both higher leaching and higher buffering capacity.

3.3.1.4 Foliar Nutrient Content. Increased foliar leaching may alter the nutrient content of leaf tissue. A significant reduction of foliar N, P, Mg, and Ca was observed in soybean leaves exposed to acid mist (Hindawi et al. 1980). Potassium content was not affected while that of S increased in these experiments. Experiments with simulated acidic rain at lower pH and soybean showed that foliar N and S increased, while Mn decreased (Brewer and Heagle 1983). The inconsistency in these two studies is typical of research in this subject area. However, the results in general, may be summarized as follows: leaching rates of micronutrients increase, there is no net effect on foliar S, and results vary for N (Torn et al. 1987). For example, the nutrient content of kidney bean and soybean foliage when exposed to simulated acidic rain applications of pH 6.0 and 3.2 demonstrated a pH-independent response (Shriner and Johnston 1981). Other studies suggest that detected effects may only be temporary.

It is suspected that energy diverted from growth may be the penalty plants pay to replace leached metabolites when exposed to simulated acidic precipitation (Amthor 1984). Nutrient reductions may also affect nutritional quality of the plant and hence, its economic value (Evans et al. 1981a; Evans 1984). In highly managed environments such as propagation beds or container nurseries where root systems are either limited or restricted, foliar leaching may lead to nutrient deficiency symptoms. However, this is not likely to occur with field crops.

3.4 EFFECTS OF WET ACIDIC DEPOSITION ON PLANT GROWTH

Plant growth may be stimulated, inhibited, or not affected by exposure to wet acidic deposition. The mechanisms by which wet acidic deposition alters plant productivity have as yet not been established. Using dose-response data, a qualitative ranking of plant growth sensitivity to simulated acidic deposition has been prepared from the current literature and is shown in Table 12 (Torn et al. 1987).

Although artificial wet acidic deposition has been shown to affect plant growth under controlled conditions, no experiments or documentation of field effects on growth were found that showed that ambient rates of acidic deposition negatively affect growth (Torn et al. 1987). The growth of many species is stimulated or not affected by simulated acidic rain in the ambient range. When the acidity dose exceeds a plant's threshold, yield of the whole plant or some portions of it is decreased. An intermediate effect between the threshold and control pH has been observed whereby the plant growth may be increased. Lee (1981) showed this intermediate effect in seed germination, seedling growth, and crop yield between pH 3.5 and 4.0. Although dose-response functions for crop yield and quality are considered an aid in predicting impacts of ambient and anticipated levels of acidity in rainfall (Troiano et al. 1982; Evans et al. 1983, 1984), the lack of linearity of such responses and the lack of understanding of their mechanisms, limits the value of the current information base.

The results of studies on the effects of simulated acidic precipitation on yield for a variety of agricultural crops are summarized in Table 12. The results clearly show no effects under field type situations except in the case of beets (Irving 1983). Root crops such as beets are the most sensitive agronomic group with low threshold and resistance for both foliar injury and yield reduction (Torn et al. 1987). All other field grown crops showed a growth peak at an intermediate pH treatment. Torn et al. (1987) concluded in their review that there was no statistical significance in the ranking of the sensitivity of agricultural crop species to increasing acidity, but that there was evidence for a decline in yield of most species at exposures to acid mist below pH 3.5, at a rate of 1 to 9% per pH unit decrease in the mist. However, exceptions were orchard grass, timothy, and possibly bluegrass, and forage crop species where yield increased between 2 and 24%. When these deviations were removed from the standardized data set examined by Torn et al., the percentage yield change for the remaining studies was -3 (± 4). Since the standard deviation is higher than the mean, the validity or reliability of the results may be questionable. The calculation was based on data from studies on legumes, forage, and grain species (Torn et al. 1987 citing Lee and Neely 1980; Lee et al. 1981; Evans et al. 1982c; and Harcourt and Farrar 1980).

Table 12. Effect of simulated acidic rain on marketable yield of roots and shoots.

Species	Marketable Yield Response to Increased Acidity	Growth Conditions	References
ROOTS			
Radish cv.Cherry Belle	no effect	F	1
Radish cv.Scarlet Knight	no effect	F	1
Radish	no effect	CE	2
Radish	decrease	CE	3
Radish	no effect	F	3
Beet	decrease	F	4
Beet	decrease	F	3
Beet cv.Detroit Dark Red	decrease	CE	5
Carrot cv.Danver's	decrease	CE	5
LEAFY			
Lettuce	decrease	CE	3
Mustard green	decrease	CE	5
Lettuce, Bibb	decrease	CE	5
Lettuce, head	decrease	CE	5
COLE			
Broccoli	decrease	CE	5
Cauliflower	no effect	CE	5
Cabbage	no effect	CE	5
TUBERS			
Potato cv.Russet	no effect	F	1
Potato cv.Kennebec	no effect	F	1
Potato cv.White Rose	decrease	CE	5
LEGUME			
Alfalfa cv.Honeoye	decrease [1]	CE	3
Alfalfa cv.Honeoye	no effect		1
Alfalfa cv.Vernal	no effect	F	6
Alfalfa cv.Vernal	increase	CE	5
FORAGE			
Ryegrass	decrease [2]	CE	7
Fescue cv.Alta	decrease [2]	F	1

CE = Controlled Environment
F = Field

[1]Decrease 1 harvest; no effect 2 harvests.
[2]Decrease after only 3 or 4 harvests

continued...

Table 12. (Concluded).

References:
1. Plocher et al. (1985)
2. Harcourt and Farrar (1980)
3. Evans et al. (1982a)
4. Troiano et al. (1982)
5. Lee et al. (1981)
6. Evans et al. (1982c)
7. Amthor and Bormann (1983)

3.5 EFFECTS OF WET ACIDIC DEPOSITION ON PLANT REPRODUCTION

Very little information is available in the current literature regarding the effects of acidic deposition on seed germination, seedling emergence, pollen viability, or fruiting (Torn et al. 1987). Seedling emergence of some woody species has been reported to be inhibited, stimulated, or unaffected by acidic precipitation (Cox 1983; Evans 1984b). Dilute acids, on the other hand, can have a scarifying effect on seed coats, thus aiding germination (Morrison 1984). Among plant species, acidity has been shown to inhibit in vitro germination of pollen of apple, grape, tomato, and camellia plants (Kratky et al. 1974; Masaru et al. 1980; and Forsline et al. 1983a). While there are no surveys of agricultural crops, estimates based upon forest research suggested a threshold for inhibition of pollen germination in trees to be pH 3.6 (Cox 1982). Comparison of foliar injury relationships suggests that pollen germination of agricultural species may be more sensitive to acidic precipitation in comparison with trees (Torn et al. 1987).

Acidic deposition may interfere with successful reproduction at different seasons and/or at different stages of development for perennial species such as fruit trees. Air pollutants may affect the fruiting process at the time of flower initiation during the first year because the inflorescence can be very vulnerable to external influences. Flowering in such plants coincides with periods of rainfall with high acidity in many regions (Forsline et al. 1983b). Alterations in the bloom can influence pollen germination and seed or fruit set, although mechanisms and responses have not been documented at this time. During the second year, air pollutants may influence fertilization, fruit set, fruit development, and maturation (Torn et al. 1987). Insect-plant interactions and pollination may also be affected due to deformed flower structure. In general, the effects of acidic precipitation on plant reproduction are still not fully understood. The effects of acidic deposition on the sexual reproduction of corn, wheat, snapbean, soybean, and other crops are currently under study at North Carolina State University by DuBay and Stucky. However, no results are available at this time.

Fruits and flowers are highly susceptible to injury, and generally sustain injury at lower levels of acidity compared with foliage (Jacobson and Van Leuken 1977; Forsline et al. 1983b; Proctor 1983; and Keever and Jacobson 1983a). Blemished fruit, if sold directly to consumers, generally has a lower market value. However, little or no change in economic value can be attributed to injury if fruit is sold for canning or extracting juice (Lee 1981). Presently there are no data relating injury on reproductive structures to alteration in reproductive potential (Torn et al. 1987).

3.6 EFFECTS OF DRY DEPOSITION ON AGRICULTURAL CROPS

The following components of dry deposition will be discussed in this section: SO_2, NOx, O_3, and H_2S.

Sulphur dioxide (SO_2) is one of the two major acid forming air pollutants in industrial emissions. It is very phytotoxic both in gaseous form and in its hydrated form when dry deposition dissolves on wet plant parts. Sulphur dioxide is extremely soluble in water under high pH. Susceptible plants may be injured by 0.05 to 0.5 ppm of sulphur dioxide after exposures as short as eight hours (Mudd and Kozlowski 1975).

Nitrogen oxides, particulary NO_2 and NO, usually are only present at phytotoxic levels in severely polluted environments. With time, the NO_2 level tends to decrease because of photochemical transformation processes that lead to ozone (O_3) production. Because of these reactions, phytotoxic levels of NO_2 are not of great concern to agricultural interests. Continuous exposure to 0.25 to 0.5 ppm of NO_2 can cause VFI in sensitive plants (Taylor and MacLean 1970; National Academy of Sciences, U.S. 1977b).

On the other hand, ozone is very phytotoxic and research into its effects on agricultural crops and plants in general has been carried out for the past thirty years. Exposure of very sensitive plants to ozone at concentrations as low as 0.10 ppm for one hour, or long term average concentrations of 0.03 ppm with periodic or intermittent episodes can be detrimental to foliage, growth, and yield. Ozone exposure of plants of intermediate sensitivity will induce injury at concentrations of 0.30 ppm for one hour, or 0.10 ppm for several hours (Guderian 1985). The threshold concentration for sensitive cultivars with respect to chronic ozone exposure has been set by the National Academy of Sciences, U.S. (1977a) as 0.05 to 0.1 ppm.

Phytotoxic levels of hydrogen sulphide have been found to be well outside the ambient range and present levels do not likely pose a threat to agricultural plant species (Heck et al. 1970). Concentrations as high as 0.3 ppm generally have no adverse effects on plants and can even stimulate growth (Torn et al. 1987). As opposed to other acid precursor gases, hydrogen sulphide can cause more injury in drier soils than under wet conditions (Thompson and Kats 1978). Because of its general lack of effect at current ambient levels, H_2S will not be discussed further in this synthesis.

3.6.1 Physiological Effects of Dry Deposition

3.6.1.1 Sulphur Dioxide Effects on Stomata. Sulphur dioxide directly affects the stomata, which may be induced to open or close depending on plant species, pollutant concentration, duration of exposure, and prevailing environmental conditions.

Sulphur dioxide induced stomatal opening has been observed in several plant species under fumigation conditions: field bean, corn, pine, bush bean, navy bean, white bean, pea, grapevine, radish, sunflower, tobacco, cucumber, soybean, and two varieties of saltbush (Torn et al. 1987). Stomatal opening occurred within a few minutes of sulphur dioxide fumigation and resulted in a 10% to 20% increase in stomatal conductance in several four-carbon (C4) species and increases as high as 200% in three-carbon species (Black 1982).

The opposite effect, stomatal closure as a result of sulphur dioxide fumigation, has been detected in a wide variety of plants. The stomata of the following tree species were induced to close under fumigation: pine, poplar, birch, and apple. A number of important agricultural species were also affected in this manner. Stomatal closure has the effect of inhibiting transpiration. The maximum transpiration inhibition rate observed in these various tree and agricultural species ranged from 35% to 75% and occurred within ten minutes to four hours following exposure, depending on the species examined (Black 1982).

The majority of the aforementioned fumigation experiments were conducted using concentrations of sulphur dioxide higher than those found in polluted environments. It is not known whether these species would show similar responses at more realistic concentration levels. Ziegler (1975), from work in polluted environments, has consistently observed increases in stomatal conductance and transpirational losses as a result of sulphur dioxide exposure. The initial increase was 15 to 20% followed by a decrease in transpiration of up to 50% in the species she studied. Ziegler further stated that low concentrations of sulphur dioxide can cause a permanent increase in transpiration. Whether the increased stomatal aperture during these exposures is caused by increased turgidity of the guard cells, a reduction in turgidity within the epidermal cells adjacent to the guard cells, or other mechanisms is as yet undetermined (Black 1982).

Once the sulphur dioxide enters the leaf through the stomata, it reaches the mesophyll cells where it is hydrolyzed in the surface fluid to become sulphite. The buffering capacity of cytoplasm decreases with time under acid conditions and especially with an increased sulphur dioxide concentration. Sulphite is toxic and therefore, is mostly oxidized to sulphate and stored. These sulphates are later converted to organic sulphur compounds or exuded by the roots. Sulphate accumulations, primarily at the edges and tips of leaves, increase with increased photosynthesis and are therefore at the maximum in young leaves. If the plant's capability to oxidize sulphites is exceeded, sulphites can build up to toxic levels and result in injury to the plant (Ziegler 1975).

3.6.1.2 Sulphur Dioxide Effects on Photosynthesis. Most studies indicate a decrease in photosynthesis with increased sulphur dioxide exposure (Mudd and Kozlowski 1975; Black 1982). Depression of photosynthesis occurs quickly and is readily reversible if the sulphur dioxide concentration drops. Responses are less reversible at higher concentrations. The lowering of the photosynthetic rate appears to be associated with breakdown of biochemical systems, tissues, and the appearance of visible foliar injury.

Sulphur dioxide induced changes in photosynthesis are also influenced by irradiance and temperature. It is hypothesized that these factors may influence the rates of detoxification or biochemical processes (Black 1982).

3.6.1.3 Sulphur Dioxide Effects on Respiration. Some investigators have shown an inhibitory effect on dark respiration as a result of exposure to high concentrations of sulphur dioxide (Gilbert 1968; Taniyama 1972). However, other investigators found stimulatory effects (Keller and Muller 1958; De Koning and Jegier 1968; Taniyama et al. 1972; Baddeley and Ferry 1973; and Black 1982). Similar conflicting results were found in studies on the effects of sulphur dioxide on photorespiration (Ziegler 1975; Koziol and Jordan 1978; and Black 1982). With these conflicting results it is not possible to derive a general conclusion on the effects of sulphur dioxide fumigation on respiration.

3.6.1.4 Nitrogen Oxide Effects on Stomata and Transpiration. There are few available data on the direct effects of nitrogen oxides on plant stomata. Indirect effects were reported by Hill and Bennett (1970) who found that NOx inhibition of photosynthesis resulted in a carbon dioxide buildup in intercellular spaces, causing the stomata to close.

After entering the plant through the stomata, nitrogen oxides diffuse through the intercellular spaces to the mesophyll and parenchyma where they react with the hydrated cell surfaces to form a mixture of nitrous and nitric acids. When these acids exceed threshold values they may cause injury to tissue (Mudd 1973; Zeevaart 1976; and McLaughlin et al. 1979).

3.6.1.5 Nitrogen Oxide Effects on Photosynthesis. Hill and Bennett (1970) found in studies on alfalfa and oats, that a concentration of 0.6 ppm of NO or NO_2 reduced carbon dioxide assimilation (a measure of photosynthetic activity). Conversely, the gases in combination showed an additive effect causing photosynthesis to be lowered further. Of the two gases, NO_2 appeard to affect photosynthesis less and allowed faster recovery than NO. Increases in photosynthesis have also been observed at low level nitrogen oxide fumigations, likely as a result of a fertilizer effect (Bull and Mansfield 1974).

3.6.1.6 Nitrogen Oxide Effects on Respiration. There are no data available concerning the direct effects of nitrogen oxides on plant respiration.

3.6.1.7 Ozone Effects on Stomata, Transpiration, and Photosynthesis.

Ozone is believed to increase the permeability of cell membranes and cause leakage of ions. Intercellularly, ozone can attack the plasmalemma of inner cell walls. This causes the permeability of the lining to be disrupted, allowing the leakage of cell contents into the intercellular spaces (Wedding and Erickson 1955; Perchorowicz and Ting 1974). Without entry to the cellular spaces, most researchers feel that ozone does not affect plants. However, experimental data on this point are contradictory.

Most researchers agree that ozone can induce stomatal closure in plants. This has the effect of inhibiting transpiration. Stomatal closure also in turn can contribute to the resistance of the plant to ozone injury (Engle and Gabelman 1966; U.S. EPA 1978).

It is generally accepted that ozone inhibits photosynthesis and that this inhibition can occur without foliar injury (Tingey 1977; U.S. EPA 1978). In addition, ozone alters the way in which the products of photosynthesis are distributed within plants (Jacobson 1982).

3.6.2 Foliar Effects of Dry Deposition

The most readily observed symptoms of gaseous pollutant exposure on plants are visible foliar injury. Foliar effects can be divided into two categories: acute and chronic.

Acute injury to plant tissue occurs within hours or days after exposure to short-term (less than 24 hours), high concentrations of pollutants. Chronic injury on plants usually develops after long-term exposure to variable, but lower, concentrations of the pollutants, with periodic, intermittent episodes.

Foliar injury caused by SO_2, NOx, and H_2S is usually found in areas near emission sources. Conversely, foliar injury due to ozone is often found on a regional scale, downwind from industrial and urban sources.

3.6.2.1 Foliar Effects of Sulphur Dioxide. Acute injury caused by sulphur dioxide is usually found as foliar necrosis in which metabolic processes cease and plant cells are killed. Chlorosis may also be observed. Chronic injury includes chlorosis in which the cells are not killed, but chlorophyll is converted to phaeophytin and leaves become bleached. The leaves remain turgid but function less efficiently (Linzon 1978).

Acute injury from sulphur dioxide exposures is caused by a rapid accumulation of bisulphite and sulphite (Linzon 1978). When the oxidation product, sulphate, accumulates beyond a threshold value that the plants can tolerate, chronic injury also occurs. Linzon (1978) estimated that sulphate is about 30 times less toxic than sulphite.

Chronic foliar injury is typified by yellowing or bronzing which may occur due to the presence of pigments previously masked by chlorophyll that has been destroyed. Chlorosis in chronic injury is generally interveinal on broad leafed plants (Torn et al. 1987).

These visual symptoms are characteristic of sulphur dioxide induced foliar injury but they can only be used as a guide in identifying the cause of injury because other factors influence plant injury as well, such as climate, insects and other pests, soil nutrition, and genetic and physiological factors. Table 13 indicates the threshold concentrations of sulphur dioxide that induce visible foliar injury for various species. The threshold SO_2 concentrations for VFI range from of 0.18 ppm for eight hours to 2.0 ppm for one hour.

The sensitivity of agricultural crops to sulphur dioxide are summarized in Table 14. Sensitivity was based on VFI with sulphur dioxide exposures under conditions favourable for gas absorption by plants (Barrett and Benedict 1970).

3.6.2.2 Foliar Effects of Nitrogen Oxide. Nitrogen dioxide is the only oxide of nitrogen that has been found to injure vegetation at concentrations found in ambient air but under very select conditions. Even when controlled fumigations of NO were conducted, visible symptoms were not seen at concentrations as high as 25 ppm (Legge et al. 1980). The middle-aged to oldest leaves were most susceptible to injury, although this varied by species.

The most commonly observed symptoms of acute nitrogen dioxide injury on broad leafed plants are interveinal water-soaked lesions on the adaxial leaf surface which appear one to two hours following exposure. These lesions rapidly collapse and bifacial necrotic areas develop. These areas are bleached to a white, light tan, or bronze colour when dry. Lesions gradually extend through the leaf to produce small irregular necrotic patches (Torn et al. 1987). This injury is similar to that seen as a result of sulphur dioxide exposure (Taylor and MacLean 1970; Taylor et al. 1975). In sensitive species, lesions occur at the margins and at the apex of leaves (Taylor and MacLean 1970). Acute injury generally occurs at nitrogen dioxide concentrations of between 1.6 to 2.6 ppm or greater for exposures of up to 48 hours (Legge et al. 1980).

Symptoms of chronic nitrogen dioxide injury include chlorosis and premature defoliation and fruit drop. An enhancement of the green colour may be observed prior to the onset of these symptoms (Taylor and MacLean 1970; Legge et al. 1980).

Van Haut and Stratmann (1967) fumigated 60 species of plants with a one:one mixture of NO and NO_2. On the basis of their results, a classification of Alberta agricultural plants as to their relative sensitivity is provided in Table 15.

Table 13. Threshold sulphur dioxide concentrations (ppm) causing foliar injury to various agricultural species.

A. Field observations	Exposure Time				
Dreisinger and McGovern (1970) (Ni/Cu smelters - Sudbury, Canada)	1 h	2 h	3 h	4 h	8 h
Sensitive crops	0.70	0.40	0.34	0.26	0.18
Intermediate	0.95	0.55	0.43	0.35	0.24
Resistant	1.88	1.1	0.86	0.70	0.49

Jones et al. (1979) (Power plants - Tennessee, US)	1 h	3 h
Sensitive	0.50 to 1.0	0.30 to 0.60
Intermediate	1.0 to 2.0	0.60 to 0.80
Resistant	2.0 +	0.80 +

B. Controlled environment fumigations					
Van Haut and Stratmann (1967)	1 h	2 h	3 h	4 h	8 h
Sensitive (rye)	2.3	1.9	1.1	-	0.75
Katz and Ledingham (1939)					
Sensitive (alfalfa, barley)	1.5	1.0	0.89	-	0.55

continued...

Table 13. (Concluded).

B. Controlled environment fumigations (continued)	Exposure Time				
Thomas (1935)	1 h	2 h	3 h	4 h	8 h
Sensitive (alfalfa)	1.2	0.71	0.55	0.48	0.36
Fujiwara (1975)					
Sensitive	-	0.60	0.45	-	0.25
Zahn (1961)					
Sensitive	0.70	0.62	0.60	0.58	0.50
Intermediate	1.2	1.1	1.0	1.0	0.9
Resistant	1.8	1.7	1.6	1.6	1.4

Adapted from the original table in International Electric Research Exchange (1981).

Table 14. Agricultural species sensitive to sulphur dioxide.[1]

Alfalfa (*Medicago sativa*)
Barley (*Hordeum vulgare*)
Bean, field (*Phaseolus vulgaris*)
Beet, table (*Beta vulgaris*)
Broccoli (*Brassica oleracea* cv. *botrytis*)
Brussel sprouts (*Brassica oleracea* cv. *gemmifera*)
Carrot (*Daucus carota* var. *sativa*)
Clover (*Melilotus* & *Trifolium* sp.)
Cotton (*Gossypium* sp.)
Lettuce (*Lactuca sativa*)
Oats (*Avena sativa*)
Radish (*Raphanus sativus*)
Rye (*Secale cereale*)
Safflower (*Carthamus tinctorius*)
Soybean (*Glycine max*)
Spinach (*Spinacea oleracea*)
Squash (*Cucurbita maxima*)
Sweet Potato (*Ipomoea batatas*)
Swiss Chard (*Beta vulgaris* cv. *cicla*)
Turnip (*Brassica rapa*)

[1]Sensitivity is based on foliar injury

Source: Barrett and Benedict (1970)

Table 15. Suggested susceptibility of various agricultural species which occur in Alberta to a combination of nitrogen dioxide and nitric oxide.

Plant Species	Sensitivity Category[1]
Alfalfa (*Medicago sativa*)	
Barley (*Hordeum distichon*)	
Crimson or Italian clover (*Trifolium incarnatum*)	Sensitive
Oats (*Avena sativa*)	
Red clover (*Trifolium pratense*)	
Maize (*Zea mays*)	
Potato (*Solanum tuberosum*)	Intermediate
Rye (*Secale cereale*)	
Wheat, common (*Triticum aestivum*)	
Cabbage (*Brassica oleracea*)	Resistant
Onion (*Allium cepa*)	

[1] Sensitivity ratings were based on Van Haut and Stratmann (1967)

The most sensitive plant species may be injured by a two-hour exposure to approximately 6.0 ppm of nitrogen dioxide under full sunlight conditions. On the other hand, under cloudy conditions injury may occur through exposures to 2.5-3.0 ppm nitrogen dioxide. It is important to note that in rural areas of Western Canada nitrogen dioxide concentrations rarely exceed 0.10 ppm and, therefore, agricultural crops and plants are rarely exposed to phytotoxic concentrations (Torn et al. 1987).

3.6.2.3 Foliar Effects of Ozone. Visible foliar injury as a result of ozone exposure is almost always confined to green foliage of plants as opposed to fruits or floral parts. The most common symptoms of VFI due to ozone as described by Hill et al. (1970) are pigmented lesions, surface bleaching, bifacial necrosis, and chlorosis.

Leaves are most sensitive to ozone injury as they reach 65% to 95% of their full size. Young leaves are generally resistant. The sensitivity of mature leaves depends on the species. Conversely, young plants are more sensitive than mature plants (Hill and Bennett 1970). Tingey et al. (1973b) reported a maximum sensitivity of soybean to ozone induced foliar injury during the end of maximum leaf expansion when stomatal resistance was low.

In fumigation experiments, ozone concentrations between 0.05 and 0.12 ppm for two hours are usually required to injure the most sensitive species. Sensitive varieties of alfalfa, spinach, clover, oats, sweet corn, and bean were injured by two hour exposures at ozone concentrations of 0.10 to 0.12 ppm (Hill et al. 1970).

3.6.3 Growth and Yield Effects of Dry Deposition

Gaseous pollutants may cause either increases or decreases in growth and yield with or without visible injury. Crop losses due to air pollutants have been reported for over 30 years. In the United States, crop losses due to air pollution are estimated to cost $1.8 billion per year (US); $1.7 billion is due to oxidants and $3.4 million is due to sulphur dioxide (Stanford Research Institute 1981).

3.6.3.1 Effects of Sulphur Dioxide on Growth and Yield. Low concentrations of sulphur dioxide can cause an increase in plant growth and yield in sulphur deficient soils. Plants normally obtain sulphur in the form of sulphate absorbed from the soil, but when soils are deficient, plants may compensate for foliar sulphur deficiency through atmospheric sources. Most researchers have found that the increases in yield in the presence of sulphur dioxide do not occur in plants grown in soils with sufficient sulphur (Faller et al. 1970; Cowling and Lockyer 1978).

In addition, a plant may also utilize the sulphate in the soil derived from dry and wet deposition. Jones et al. (1979) reported that atmospheric sulphur is a major contributor to the needs of agronomic and horticultural crops as a plant nutrient in South Carolina. Because soils are generally sulphur deficient and because commercial fertilizers are quite expensive, atmospheric sulphur could be an important nutrient source for farmers (Prince and Ross 1972).

Several studies have shown significant decreases in growth and yield due to sulphur dioxide (Guderian 1977; Crittenden and Read 1978a,b; Heagle and Johnston 1979; Davies 1980; Irving et al. 1982; Noggle and Jones 1982; and Heagle et al. 1983b).

The effects of sulphur dioxide from a nearby industrial source on the yield of barley and alfalfa (at concentrations between 0.015 to 0.082 ppm (mean concentration over three growing seasons) are shown in Table 16. At the highest concentration, barley yield decreased by 34.9% and alfalfa yield by 30.3% when compared with the control (Warteresiewicz 1979, cited in Godzik and Krupa 1982).

Guderian and Stratmann (1968) studied the effects of ambient sulphur dioxide on various agricultural crops near an iron ore roasting plant. Their results indicated that at an average sulphur dioxide concentration of 0.08 ppm, plant yields decreased by as much as 9.1% for canola and 44.4% for winter wheat.

In similar studies, Maly (1974, cited in Godzik and Krupa 1982) reported decreases in yield of 8.1 to 23.3% for various crops (Table 17). Of significance is that although the pollutant concentrations in Maly's study were higher than those of Guderian and Stratman (1968) yield reductions were of similar magnitude.

Response to a pollutant can differ among cultivars of the same species. Laurence (1979) exposed seven varieties of wheat to various concentrations of sulphur dioxide. The results of this experiment are shown in Table 18. At low SO_2 concentrations, Laurence showed that yields increased, but as concentrations increased the cultivars responded with decreased yields. However, significant yield reductions were not observed at commonly occurring dosage levels.

3.6.3.2 Effects of Nitrogen Oxide on Growth and Yield. Nitrogen dioxide in low concentrations can assume the role of a fertilizer and be a source of necessary nitrogen for the plant. Investigators have reported increases in plant growth and yield with low concentration nitrogen dioxide exposures. This fertilizer effect has been observed in both nitrogen deficient and in nitrogen sufficient soils (Cowling and Koziol 1982). Concentrations of 0.05 ppm nitrogen dioxide maintained continuously can cause small reductions in growth and yield for sensitive agricultural species (Taylor et al. 1975).

The results of most of the studies conducted on nitrogen dioxide below 1.0 ppm have shown inconclusive effects on growth and yield of agricultural plants. Spierings (1971) studied the effects of nitrogen dioxide at a concentration of 0.25 ppm on the yield and growth characteristics of tomato over a 128 day growing season. He found that there was a 22% decrease in fresh weight of the plants, a 12% decrease in average weight of the fruits, and an 11% decrease in fruit number, as well as smaller leaves, petioles, and stems. After 49 days at 0.25 ppm or at concentrations of 0.50 ppm after 10 days, the plants grew tall and had thinner stems and smaller leaves. It is important to note that the NO_2 concentrations used in many of these experiments are seldom found under ambient conditions.

3.6.3.3 Effects of Ozone on Growth and Yield. The phytotoxicity of ozone was firmly established in 1957 (U.S. EPA 1978). Ozone has been shown to reduce growth and yield of many agricultural species.

The lowest limit for injury resulting from ozone exposure follows long term average concentrations of 0.02 to 0.05 ppm with periodic intermittant peaks, for most species under general conditions (Guderian 1985). Results of experiments using acute exposures of ozone are summarized in Table 19. The exposures in these experiments varied in concentration from 0.05 to 1.0 ppm and an exposure time from one to 24 hours.

Table 16. Yields of two field crops grown in different concentrations of sulphur dioxide.

Approximate SO_2 Concentration (ppm)	Percent Yield: Barley Grain	Alfalfa Forage
.015	100.0	100.0
.029	98.0	99.2
.036	94.0	98.2
.038	92.2	100.4
.040	90.2	98.6
.047	85.9	88.0
.058	79.7	85.7
.060	76.3	82.0
.062	71.8	76.3
.068	70.6	78.3
.079	64.7	70.0
.082	65.1	69.7

Source: Warteresiewicz (1979), cited by Godzik and Krupa (1982)

Table 17. Yield of various crops in field plots exposed to sulphur dioxide.

Species:	Decrease in Yield (%)
Oats, grain	12.2
Oats, straw	8.1
Clover	15.5
Cereals[1] (wheat, barley, rye & oats)	20.0
Potatoe	16.2
Flax (seed, fibre)	28.3, 23.8

Concentration: 1.26 ppm to 1.37 ppm (weekly averages)

Decrease in yield is relative to control

[1]Data from a different growing season

Source: Maly (1974), cited by Godzik and Krupa (1982)

Table 18. Effects of sulphur dioxide on cultivars of hard red spring wheat (HRS) and soft white winter wheat (SWW).

Cultivar	Concentration (ppm)	Dry Weight After Exposure For: 30 h	78 h	100 h
Era (HRS)	0.0	0.089	0.112ab*	0.095ab
	0.2	0.113	0.138a	0.114a
	0.4	0.101	0.099ab	0.098ab
	0.6	0.105	0.084b	0.076b
Waldron (HRS)	0.0	0.168	0.164	0.152ab
	0.2	0.178	0.215a	0.173a
	0.4	0.142	0.165b	0.135ab
	0.6	0.159	0.127b	0.108
Thatcher (HRS)	0.0	0.127	0.144	0.132ab
	0.2	0.144	0.182	0.166a
	0.4	0.125	0.143	0.127ab
	0.6	0.130	0.140	0.092b
Prelude (HRS)	0.0	0.165	0.167	0.168
	0.2	0.179	0.207	0.186
	0.4	0.138	0.172	0.164
	0.6	0.171	0.156	0.122
Arrow (SWW)	0.0	0.146	0.201b	0.159ab
	0.2	0.163	0.268a	0.178a
	0.4	0.178	0.197b	0.138ab
	0.6	0.167	0.148b	0.117b
Ticonderoga (SWW)	0.0	0.156	0.154	0.151ab
	0.2	0.147	0.172	0.174a
	0.4	0.149	0.158	0.153ab
	0.6	0.136	0.126	0.103b
Yorkstar (SWW)	0.0	0.162	0.145	0.157a
	0.2	0.154	0.158	0.177a
	0.4	0.161	0.145	0.145ab
	0.6	0.141	0.120	0.095b

* Means followed by the same letter are not significantly different (P=0.05) based on Tukey's test for comparison of means. Absence of letters indicates no significant difference. All comparisons are made within one cultivar type and exposure period. Mean of 8 plants.

Adapted from the original table in Godzik and Krupa (1982)

Source: Laurence (1979)

Table 19. Effects of acute ozone exposure on growth and yield of agricultural crops.

Plant Species	Ozone Concentration (ppm)	Exposure Time (h)	Plant Response[1] Percent Reduction	Reference
Cucumber				
cv. Ohio Mosaic	1.0	1	19, top dry wt	1
	1.0	4	37, top dry wt	
Grapevine (*Vitus labrusca*)				
cv. Ives	0.08	4	60, shoot growth	2
cv. Delaware			33, shoot growth	
Pinto bean	0.05	24	Significant reduction in leaf growth	3
	0.10	12	Significant reduction in leaf growth	
Onion				
cv. Sparan Era	0.20	24	0, no effect	1
	1.0	1	19, plant dry wt	
	1.0	4	49, plant dry wt	
Potato				
cv. Norland	1.0	4	0, tuber dry wt	1
		4(3X)	30, tuber dry wt	
Radish				
cv. Cavalier	0.25	3	36, top dry wt	4
cv. Cherry Belle	0.25	3	38, root dry wt	
Radish	0.40	1.5(1X)	37, root dry wt	5
		1.5(2X)	63, root dry wt	
		1.5(3X)	75, root dry wt	
Snap bean	0.30	1.5 (2X)	10, plant dry wt	6
			12, pod dry wt	
	0.60	1.5 (2X)	25, plant dry wt	
			41, pod dry wt	

continued...

Table 19. (Concluded).

Plant Species	Ozone Concentration (ppm)	Exposure Time (h)	Plant Response[1] Percent Reduction	Reference
Soybean	0.30 to 0.45	1.5	Threshold for reduction of shoot growth	7
Tall fescue (*Festuca arundinacea*) cv. Kentucky 3	0.30	2 (3X)	22, shoot dry wt	8
Tobacco cv. Bel W3	0.30	2	48, chlorophyll content	9
Tomato cv. Fireball	0.5	1	15, plant dry wt (grown in moist soil)	10
	1.0	1	20, plant dry wt (grown in moist soil)	
	0.5	1	+15, plant dry wt (grown in dry soil)	
	1.0	1	+25, plant dry wt (grown in dry soil)	
White clover (*Trifolium repens*) cv. Tillman	0.30	2	17, shoot dry wt 33, root dry wt	8

[1] Responses marked with "+" are increases

References:
1. Ormrod et al. (1971)
2. Shertz et al. (1980)
3. Evans (1973)
4. Adedipe and Ormrod (1974)
5. Tingey et al. (1973a)
6. Blum and Heck (1980)
7. Heagle and Johnston (1979)
8. Kochhar et al. (1980), cited by Guderian (1985)
9. Adedipe et al. (1973)
10. Khatamian et al. (1973)

Various experiments on the effects of chronic exposure to ozone on agricultural crops have been conducted and the results are summarized in Table 20.

3.6.4 Effects of Dry Deposition on Plant Reproduction

Dry deposition is suspected of having direct effects on plant reproductive structures and processes. Unfortunately, aside from several studies on pollen germination, there has been little research on sulphur dioxide effects on plant reproduction. A similar situation exists regarding the specifics of the reproductive effects of nitrogen dioxide, although it has been known for several years that this gas causes detrimental effects on reproductive structures of vegetation.

Pollen germination can be affected by sulphur dioxide exposure. Fumigations at 10 ppm for six days, with Swiss mountain pine and Scots pine pollen, caused a reduction in germination and induced pollen tubes to burst when tests were run on a moist soil medium (Dopp 1931). However, when these tests were run using a dry medium, no effects were detected. Availability of moisture likely caused the formation of acids in the presence of sulphur dioxide because without this moisture dry deposition did not appear to cause a detrimental plant response, at least in these studies.

Decreases in the yield of fruits and seeds have been observed by several investigators as a result of nitrogen dioxide fumigations (Taylor et al. 1975; Irving et al. 1982; and Whitmore and Mansfield 1983). However, the specific numerical descriptors of cause-effect relationships for these results are not available.

Ozone has been shown to cause decreases in grain or seed yield, number and weight of fruit, and to delay fruit set. The aforementioned direct effects of ozone can be found regardless of whether or not foliar injury (VFI) occurs (National Academy of Sciences, U.S. 1977a; Bonte 1982; and Jacobson 1982).

Hydrogen sulphide at very low concentrations (0.07 ppm) caused a reduction in catalase activity, seed germination, and size of the fruiting structure in brussel sprouts (Dobrovolsky and Strikha 1970). Sprouts also showed signs of chlorosis. On the basis of their results the authors concluded that in comparison with sulphur dioxide toxicity, hydrogen sulphide was: ten times more toxic to seed germination; three times more toxic to leaflet formation; two times more toxic with respect to sprout size; and fifty times more inhibitory to catalase activity.

3.7 EFFECTS OF MIXTURES OF GASEOUS POLLUTANTS ON CROPS

The joint effects of pollutants on crops can be described as follows:

1. If the plant response equals the sum of the effects of the individual pollutants, it is termed an additive response;
2. If the plant response to the combination of pollutants is greater than the sum of the response to the individual pollutants, it is termed as a more than additive response;
3. If the plant response to the combination of pollutants is lesser than the sum of the response to the individual pollutants, it is termed as a less than additive response.

Table 20. Effects of long-term controlled ozone exposures on growth, yield, and foliar injury of various agricultural species.

Species	Ozone Conc. (ppm)	Exposure Hrs d^{-1}/days	Plant Response (% Reduction or Injury from Control)	Ref.
Alfalfa	0.10	2 / 21 days	16, top dry wt	1
	0.15	2 / 21 days	26, top dry wt	
	0.20	2 / 21 days	39, top dry wt	
Alfalfa	0.05	7 / 68 days	30, shoot dry wt, 1st harvest 50, shoot dry wt, 2nd harvest	2
Bean, pinto	0.13	8 / 28 days	79, top dry wt 73, root fresh wt 70, height	3
Bean, pinto	0.05	24 / 3-5 days	50, leaf chlorosis	4
	0.05	24 / 5 days	(fivefold increase in lateral bud elongation)	
Bean, pinto	0.15	2 / 63 days	33, plant dry wt 46, pod fresh wt	5
	0.25	2 / 63 days	95, plant dry wt 99, pod fresh wt	
	0.35	2 / 63 days	97, plant dry wt 100, pod fresh wt	
Bean, pinto	0.15	2 / 14 days	8, leaf dry wt	6
	0.15	3 / 14 days	8, leaf dry wt	
	0.15	4 / 14 days	23, leaf dry wt	
	0.15	6 / 14 days	49, leaf dry wt	
	0.225	2 / 14 days	44, leaf dry wt	

continued...

Table 20. (Continued).

Species	Ozone Conc. (ppm)	Exposure Hrs d^{-1}/days	Plant Response (% Reduction or Injury from Control)	Ref.
Bean, pinto	0.225	4 / 14 days	68, leaf dry wt	6
	0.30	1 / 14 days	40, leaf dry wt	
	0.30	3 / 14 days	76, leaf dry wt	
Bean, pinto	0.06	5 days/week 40 days	48, shoot dry wt 50, root dry wt	7
Beet	0.20	3 / 38 days	50, top dry wt 40, storage root dry wt 67, fibrous root dry wt	8
Crimson clover	0.03	8 / 6 weeks	<10, dry wt	9
Corn, sweet cv. Golden	0.20	3 / 3 days/wk until harvest	13, kernel dry wt 20, top dry wt 48, root dry wt	10
	0.35	3 / 3 days/wk until harvest	20, kernel dry wt 48, top dry wt 54, root dry wt	
	0.05	6 / 64 days	9, kernel dry wt 14, leaf injury	
	0.10	6 / 64 days	45, kernel dry wt 25, leaf injury	
Fescue, tall	0.09	6 weeks	17, leaf dry wt 15, shoot dry wt	12
Orchard grass	0.09	4 / 5 days/wk 5 weeks	14 to 21, shoot dry wt	13
Perennial ryegrass	0.09	4 / 5 days/wk 5 weeks	14 to 21, shoot dry wt	13

continued...

Table 20. (Continued).

Species	Ozone Conc. (ppm)	Exposure Hrs d^{-1}/days	Plant Response (% Reduction or Injury from Control)	Ref.
Potato (2 seasons)	0.20	3 h (6X) 2 / week		14
cv. Norland:			30, tuber wt/19, tuber no.	
			20, tuber wt/21, tuber no.	
cv. Kennebec:			54, tuber wt/40, tuber no.	
			30, tuber wt/32, tuber no.	
Potato	0.05 (>or =)	326 to 533 total hours two years	34 to 50. tuber fresh wt	15
Radish	0.05	8 / 5 days/wk 5 weeks	54, root fresh wt	16
Ryegrass, Italian	0.09	8 / 6 weeks	36, dry wt	
Soybean	0.05	6 / 133 days	3, seed yield 22, plant fresh wt 19, injury	
Spinach	0.06	7 / day 37 days	18, fresh wt	18
	0.10		37, fresh wt	
	0.13		69, fresh wt	
Soybean	0.064	9 / 55 days	31, seed dry wt	18
	0.079		45, seed dry wt	
	0.094		56, seed dry wt	
Soybean	0.05 (>or=)	465 / growing season	28, seed wt	19

continued...

Table 20. (Concluded).

Species	Ozone Conc. (ppm)	Exposure Hrs d^{-1}/days	Plant Response (% Reduction or Injury from Control)	Ref.
Tomato	0.20	2.5 / 3 days/wk 14 weeks	1, yield 32, top dry wt 11, root dry wt	10
	0.35	2.5 / 3 days/wk	45, yield; 72, top dry wt 59, root dry wt 8, tillering	
Wheat	0.20	4 / 7 days (anthesis)	30, yield	20
Wheat, winter	0.10	7 / 54 days	16, seed dry wt	21
	0.13	7 / 54 days	33, seed dry wt	

References:

1. Shinohara et al. (1974)
2. Neely et al. (1977)*
3. Manning et al. (1971a)
4. Engle and Gabelman (1966,1967)
5. Hoffman et al. (1973)
6. Maas et al. (1973)
7. Manning (1978)*
8. Ogata and Maas (1973)
9. Bennett and Runeckles (1977)
10. Oshima (1973)
11. Heagle et al. (1972)
12. Johnston et al. (1980)*
13. Horsman et al. (1980)*
14. Pell et al. (1980)*
15. Heggestad (1973)
16. Tingey et al. (1973a)
17. Heagle et al. (1974)
18. Heagle et al.(1979a)*
19. Kress and Miller (1981)*
20. Shannon and Mulchi (1974)
21. Heagle et al. (1979b)*

* References cited by Guderian (1985)

In sequential exposures, plants may become sensitized or tolerant to a pollutant by a previous exposure to a different pollutant (Guderian 1985). Changes in injury type may also occur in plants exposed to pollutant mixtures compared with single pollutants. Plant responses to pollutant mixtures depend on many factors including components of the mixture, temporal succession, and factors that influence a plant's response to single pollutants.

Sulphur dioxide from fuel combustion and ozone produced photochemically are the two pollutants most frequently studied as mixtures. Because nitrogen dioxide is also produced during combustion, it is also considered in certain studies on pollutant mixtures. The potential for more than additive responses from mixtures of ozone, sulphur dioxide and nitrogen dioxide is considered to be the most important pathway for atmospheric interaction between plants and nitrogen dioxide (Taylor 1984).

Mechanisms for plant injury as a result of exposure to gaseous pollutant mixes are not well understood, but it is assumed that the processes that govern plant responses to single pollutants would hold (Guderian 1985). There does not seem to be any direct correlation between visible symptoms and growth effects in plants exposed to gaseous mixtures in contrast to the studies on single gaseous pollutants (Tingey et al. 1971a,b, 1973a,b; Mandl et al. 1973). It has been observed that growth of roots is inhibited more than growth of other plant parts by exposures to gas mixtures, again in contrast to effects documented for single gaseous pollutants (Ormrod 1984).

3.7.1 Combined Effects of Sulphur Dioxide and Ozone

Studies by Beckerson and Hofstra (1979a,b) on radish, cucumber, and soybean exposed to sulphur dioxide and ozone both singly and in combination showed that stomatal conductance was stimulated by SO_2, inhibited by O_3, and inhibited to a greater degree by the mixture. The concentration of each gas singly, or in the mixture, was 0.15 ppm.

Most of the studies on foliar injury due to sulphur dioxide and ozone have indicated a less than additive effect. Few other studies, however, have shown more than additive foliar effects of mixtures of the two gases.

In a number of studies, mixtures of sulphur dioxide and ozone have produced more than additive effects on growth and yield at concentrations at or below a given threshold. The yields of soybean, radish, and tobacco were found to respond additively to a mixture of SO_2 and O_3 at concentrations of each between 0.05 and 0.10 ppm (Tingey et al. 1971a, 1973c). Soybean root fresh weight was suppressed more than additively by the pollutant mixture in this study. Other studies have also found the responses of plants to mixtures of sulphur dioxide and ozone to be more than additive: snapbean and tomato (Heggestad and Bennett 1981; Shew et al. 1982), or additive: potato, fescue, soy beans (Flagler and Younger 1982; Foster et al. 1983; and Heagle et al. 1983b).

3.7.2 Combined Effects of Sulphur Dioxide and Nitrogen Dioxide

Because ambient concentrations of nitrogen dioxide rarely approach the injury thresholds for plants, its potential joint effects with other pollutants are a primary concern. A majority of researchers have reported either additive or more than additive

effects in plants as a result of exposures to mixtures of sulphur dioxide and nitrogen dioxide (Tingey et al. 1971b; Hill et al. 1974; Irving et al. 1982; Reinert and Sanders 1982; and others). A few investigators have also observed less than additive plant responses (Thompson et al. 1980; Reinert and Sanders 1982; and Whitmore and Freer-Smith 1982).

Photosynthesis was shown to be initially stimulated in pea plants exposed to a nitrogen dioxide/sulphur dioxide mixture; however, this effect was reversed leading to inhibition within a short period of time (Bull and Mansfield 1974). Similarly, NO_2-SO_2 mixtures were found to decrease transpiration in bean plants at concentrations of 0.1 ppm each even though individually these gases caused a stimulatory effect (Ashenden 1979).

Tingey et al. (1971b) observed more than additive injury on the adaxial surface of leaves in plants exposed to a mixture of sulphur and nitrogen dioxides. This effect differed greatly from the effects produced by either gas alone or from symptoms generally produced by ozone. The visible injury threshold for the most sensitive agricultural species with sulphur dioxide and nitrogen dioxide mixtures was between 0.05 and 0.10 ppm of each gas (Tingey et al. 1971b).

Ashenden and Mansfield (1978) exposed four grass species to a mixture of sulphur and nitrogen dioxide in long-term experiments using concentrations of 0.068 ppm each. They observed a more than additive reduction, in the total dry weight of orchard grass, Italian ryegrass, and timothy. In the case of Kentucky bluegrass, Ashenden and Mansfield (1978) also found an additive growth reduction. Other studies on the joint effects of sulphur dioxide and nitrogen dioxide on plants have shown: as a time series of growth, more than additive, additive, or less than additive effects on the dry weight of grass roots (Whitmore and Freer-Smith 1982); a more than additive reduction in seed production in soybean (Irving et al. 1982); a less than additive reduction in root and shoot weight in marigolds (Reinert and Sanders 1982); a general additive reduction of growth and yield in desert plant species but in some instances, also less than additive effects (Thompson et al. 1980).

Research on the joint effects of sulphur dioxide and nitrogen dioxide on plant reproduction is limited. Masaru et al. (1976) have shown that pollen tube growth can be reduced more than additively in lilies exposed to SO_2:NO_2 at concentrations of 0.24:0.12 ppm for 30 to 60 minutes.

From the literature review, it is evident that the physiological effects of mixtures of sulphur dioxide and nitrogen dioxide on plants is not well understood. What is known indicates that effects are species specific and often quite different from the responses to individual pollutant exposures.

3.7.3 Combined Effects of Nitrogen Dioxide and Ozone

Very few studies have been conducted on the effects of mixtures of nitrogen dioxide and ozone on plants. More than additive, additive, and less than additive interactions have been documented with respect to foliar injury (Torn et al. 1987). The temporal sequencing of exposures to NO_2 and O_3 has been shown to be important. In one study, increased sensitivity of plants to ozone was observed as a result of previous exposure to nitrogen dioxide. This resulted in reduced growth and yield (Runeckles et al. 1978). While not immediately relevant to crops, studies on growth and biomass in

trees exposed to mixtures of nitrogen dioxide and ozone have produced a variety of results ranging from more than additive growth suppression (height growth in Virginia and Loblolly pine) to less than additive suppression of root accumulation in sweet gum and total dry weight in white ash (Kress and Skelly 1982).

3.7.4 Combined Effects of Sulphur Dioxide, Nitrogen Dioxide, and Ozone

Studies on the joint effects of sulphur dioxide, nitrogen dioxide, and ozone are in the initial phases and little definitive documentation exists at this time (Torn et al. 1987).

Foliar injury similar to that observed with ozone alone has been observed when plants were exposed to the combination of the three pollutants (Torn et al. 1987). The effects on growth and yield of sulphur dioxide, nitrogen dioxide, and ozone have not been thoroughly studied. Researchers have found that in nearly every instance, exposure to the three pollutants caused a greater loss in plant growth and yield than exposure to a single or a mixture of two pollutants. Studies conducted thus far are important because they have shown that growth and yield responses to the three pollutant mixture occur in the nitrogen dioxide concentration range of 0.05 to 0.30 ppm, i.e., within the ambient concentrations of nitrogen dioxide at certain locations (Torn et al. 1987). The decrease in growth and yield caused jointly by nitrogen dioxide with sulphur dioxide and/or ozone varied from 5% to 20% at concentrations of nitrogen dioxide that cause little or no injury when that pollutant was used singly (Reinert 1984).

3.8 COMBINED EFFECTS OF DRY AND WET DEPOSITION

The joint effects of dry and wet deposition are considered to be significant since both processes contribute to the pollutant burden. Research to date suggests that more than additive or additive effects on plant processes and foliar injury can occur as a result of exposure to both types of deposition (Torn et al. 1987).

Experiments using various ozone concentrations and simulated acidic precipitation with differing pH values produced an additive response in foliar injury and reduction of chlorophyll in young leaves of radish (Shriner 1983). Older leaves in the same experiment exhibited a more than additive foliar injury response. Similar results were reported by Shriner (1983) for simulated acidic precipitation and sulphur dioxide. On the contrary, experiments conducted by Norby and Luxmoore (1983) on soybean exposed to simulated acidic rain and a gaseous mixture of ozone and sulphur dioxide showed no foliar injury effects. The effects of of wet and dry deposition on growth and yield have been studied by Shriner (1978, 1983) and Irving and Miller (1981). These studies showed either additive or more than additive plant responses to combinations of wet and dry deposition, depending on the species studied.

3.9 EFFECTS OF ACIDIC DEPOSITION ON PLANT-SOIL INTERACTIONS

The effects of wet and dry deposition on soils have been fully discussed in an earlier section and will only be treated here as they relate directly to plants and agricultural practices.

Short-term impacts of acidic rain or gaseous pollutants on agricultural soils will be small on intensively managed systems (Coleman 1983; McFee 1983; Mortvedt 1983;

and Torn et al. 1987). At current or projected levels of ambient acidity, N and S deposited in acidic rain will act as fertilizer supplements rather than as toxins on soils of all degrees of management (Jones and Suarez 1979; Sandhu et al. 1980). The greater potential for toxicity relates to the free hydrogen concentration of acidic rain. However, current agricultural practices have a much greater effect on soil pH than does atmospheric deposition. Estimates are that the H^+ flux from heavily acidified rain would be only 1% of the total flux available from nitrogen fertilizers (Plocher et al. 1985).

On less intensively managed lands, acidic precipitation could have a significant effect on soil quality and the overall fertility of the soil. While acidification is prevented or managed on agricultural soils, it is essentially irreversible in uncultivated soils without excessive expenditure (McFee 1980). Generalized responses of the soil environment to natural or anthropogenic changes in soil pH are summarized in Figure 1 (Brady 1974). The most likely changes in soil characteristics that could result from acidic deposition are: increase in the acidity of soil solution; increase in exchangeable aluminum and other heavy metals; and a change in the composition of the exchangeable ion complex with a concomitant decrease in base saturation capacity (Russell 1973; Agrawal et al. 1985).

Very few investigators have addressed the potential for acidic deposition induced changes in plant growth, in the context of the interactions of the plant with the soil. A possible exception is symbiotic systems in roots (Torn et al. 1987).

3.9.1 Effects of an Acidified Soil Environment on Plants

The threshold for direct toxicity to plants from the acidity of soil solution is pH 3.0 (Russell 1973). Before the soil becomes this acidic, related changes in the soil will render the soil unsuitable for most crops; these secondary effects are the primary route by which soil acidity is harmful (Russell 1973). High aluminum concentration is the most common cause of crop failure on acidic soils (Russell 1973). Aluminum can harm plants in two ways. Aqueous aluminum in free spaces of the root surface may inhibit root uptake of phosphates, and sugar phosphorylation may be inhibited by intercellular aluminum. Manganese toxicity can also result from increased acidity (Russell 1973). Tables 21 and 22 indicate the concentrations of various heavy metals toxic to plants and plant sensitivity to such metals under acidity induced soil conditions.

Overall soil acidity also has an effect on the ability to grow certain crops. Table 23 shows the recommended crops for Great Britain under varying soil pH. Table 24 shows the effects of reduced soil pH on the yield of barley and alfalfa.

3.9.2 Effects of Altered Soil Acidity on Soil Organism-Plant Interactions

The pH of the soil influences the success of soil-borne organisms which can either be beneficial or harmful to plants. Some soil organisms are at an advantage in acidic soils, whereas others are inhibited. Therefore, the net effect of acidic deposition or gaseous pollutant exposure on plant health will encompass four factors: (1) the deleterious effects on commensals or symbionts; (2) the stimulation or inhibition of pests; (3) the stimulation or inhibition of plant health; and (4) the effects of altered plant biochemistry on plant-organism interactions.

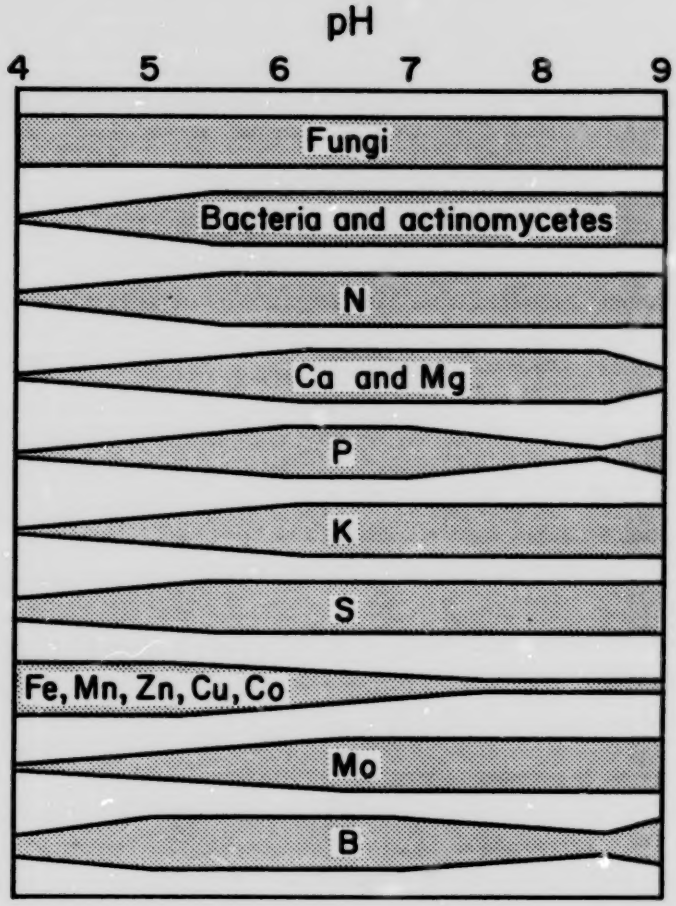

Figure 1. Relationship between soil pH and activity of microorganisms and availability of plant nutrients.
Source: Brady (1974)

Table 21. Toxic concentration of copper, nickel, or zinc in leaf tissue.

Species	(ppm) Cu	Ni	Zn
Spring barley	19	12	210
Ryegrass	21	14	221
Lettuce	21		
Canola	16		
Wheat	18		

Source: Davis and Beckett (1978)

Table 22. Plant sensitivity to acid-induced changes in the soil environment.

Aluminum tolerance	Oats >> potatoes >> beets
Manganese tolerance	Oats >> beets >> potatoes
Calcium demand	Beets = potatoes >> oats

Source: Russell (1973)

Table 23. Recommended crops for soils with varying acidity in Great Britain.

Soil Acidity	Crops Recommended
Neutral to low acidity	Alfalfa Barley Sugar beet
Medium acidity	Peas Red clover Wheat
High acidity	Oats Rye White clover

Source: Russell (1973)

Table 24. Effect of drop of 0.1 unit in soil pH on barley and alfalfa yield.

Crop	Initial pH Range	Reduction in Yield
Barley	5.2 - 5.5	161 kg/ha
Alfalfa	5.5 - 6.0	448 kg/ha

Source: Sandhu et al. (1980)

3.9.2.1 Effects of Acidic Deposition on Plant-Microbe Interactions. The effects of acidic precipitation and gaseous dry deposition on the life cycles of pathogens, on plant vulnerability to pathogens, and on plants as hosts for beneficial organisms is a topic of intensive study in agriculture. Table 25 provides a comprehensive listing of experiments conducted with the major gaseous pollutants and acid precipitation on agricultural crops and their pathogens.

3.9.2.2 Effects on the Plant as Host Organism. Certain characteristics of the host-pathogen relationship appear to be sensitive indicators of the overall stress on the plant due to gaseous and aqueous pollutants (Shriner 1980). Pollutants may alter the primary metabolites, affect the digestibility of the host and the feeding behaviour of insects (Hughes 1983). For example, Mexican bean beetles developed more slowly and were less fecund when feeding on plants fumigated with hydrogen fluoride (Hughes 1983). Pollutants may reduce the ability of the plant to produce defensive chemicals. Production of protective chemicals may also be reduced or increased by insect injury to the plant (Hughes 1983; Schultz and Baldwin 1982, respectively). Therefore, plant injury symptoms must be carefully examined before assuming a cause-effect relationship as a result of acidic deposition.

3.9.2.3 Effects on Viruses, Fungi, and Bacteria. Stimulation or inhibition of growth and reproduction due to acidic precipitation has been shown to vary widely for soil bacteria, yeasts, and fungi. Bacteria are the least resistant to acidity (activity below pH 5.6 is reduced and is almost zero at pH 4.0 (Brady 1974, Figure 7), while fungi are the most tolerant (Shriner 1978). Table 26 summarizes information on the stages in the life cycles of fungi with the potential for the greatest interference by acidic pollutants.

Hughes and Laurence (1983) reported that viruses are more successful on plants exposed to air pollution. Conversely, in the studies conducted by Laurence (1981) and Hughes and Laurence (1983), viral infection provided protection to plants exposed subsequently to ozone. The incidence and severity of diseases caused by obligate fungal parasites can also be reduced by exposure to ozone (Hughes 1983). Hughes also found that multiple exposures to sub-acute concentrations of ozone increased the success of powdery mildew on barley plants. Air pollution stress may increase the incidence and severity of diseases induced by non-obligate fungal parasites (Laurence 1981). This is considered to be important since these are numerous, widely distributed facultative parasites often associated with important agricultural crops (Laurence 1981).

3.9.2.4 Effects on Insect-Plant Relationships. In discussing research on pollutant-plant-insect interactions, Hughes (1983) noted that sulphur dioxide stimulated growth and reproduction of the milkweed bug, as did carbon monoxide and nitric oxide. Feir (1978) concluded that feeding insects are relatively unaffected by contact with gaseous pollutants such as ozone, but are significantly affected by water-soluble pollutants such as acidic sulphate aerosols.

Beetles were found to be more fecund and grew to a larger size in fields of soybean exposed to sulphur dioxide (Hughes et al. 1981, 1982; Hughes 1983). Hughes

Table 25. Effect of pollutants on plant-pathogen interactions.

Plant/Pathogen	Exposure[1]	Effect on Pathogen Induced Disease	Effect on Pollutant Injury on the Plant	Ref.
OZONE				
Barley/ *Erysiphe graminis*	S	Reduced infection from exposed spores, colony size reduced. Multiple exposure caused increases in colony size.	-	1
Wheat/ *Puccinia graminis*	S	Reduced sporulation.	-	2
Oats/*P. coronata*	S	Reduced sporulation.	-	2
Oats/*P. coronata*	S	Reduced growth of uredia.	-	3
Wheat/*P. graminis*	A	Decreased growth of hyphae. Decreased number of spores. Reduced infection.	-	4
Wheat/*P. graminis*	A	-	Reduced O_3 sensitivity.	5
Corn/ *Helminthosporum maydis* Race T	S	a) 18 pphm increased colony size b) 12 pphm increased number of spores	-	6
Geranium/*Botrytis cinerea*	A	Reduced sporulation. Reduced infection by exposed spores.	-	7
Geranium/*B. cinerea*	A	Flocculent material produced.	-	8
Broad bean/*B. cinerea*	-	-	Reduced O_3 sensitivity.	9
Potato/*B. cinerea*	-	Increased disease development. Predisposition to infection.	-	10
Geranium flowers/ *B. cinerea*	A	Reduced disease development.	-	11
Geranium leaves/ *B. cinerea*	A	Increased disease development.	-	12
Poinsettia/ *B. cinerea*	A	No effect on disease development.	-	9
Pinto bean/Root inhabiting fungi	A	Increased number of fungal colonies. Decreased nodulation.	-	13
Cabbage/*Fusarium oxysporium*	S	Decreased disease development slightly.	-	14
Rose/*Diplocarpon rosae*	S	Reduced disease development.	-	4

continued...

Table 25 (Continued).

Plant/Pathogen	Exposure[1]	Effect on Pathogen Induced Disease	Effect on Pollutant Injury on the Plant	Ref.
OZONE				
Tobacco/Tobacco mosaic virus	F	-	Reduced O_3 sensitivity.	15
Tobacco, Pinto bean/ Tobacco mosaic virus	A	-	Reduced O_3 sensitivity.	16
Pinto bean/bean common mosaic virus	A	-	Reduced O_3 sensitivity.	12
Pinto bean/alfalfa mosaic virus, tobacco ringspot virus, tobacco mosaic virus, tomato ringspot virus	A	-	Reduced O_3 sensitivity.	13
Tobacco/Tobacco etch virus	A	-	Reduced O_3 sensitivity.	17
Tobacco/Tobacco streak virus	A	-	Increased O_3 sensitivity.	18
Soybean/*Rhizobium japonicum*	A	Root growth and nodulation reduced.	-	19,20
Alfalfa/*Xanthomonas alfalfa*	A	Reduced disease development.	Reduced O_3 sensitivity.	21
Kidney bean/*Pseudomonas phaseolicola*	A		Reduced O_3 sensitivity in halo.	22
Soybean/*Pseudomonas* sp.	A	Increased and modified Hypersensitive reaction (HR) (Pre-exposure inoculation). No HR (Post-exposure inoculation).	Inoculation 24 h before exposure prevented O_3 injury.	23
Soybean/*P. glycinea*	A	Reduced disease incidence.	No effect.	24
Wild strawberry/ *Xanthomonas fragaiae*	A S	Reduced disease incidence. No effect.	No effect.	25
SULPHUR DIOXIDE				
Wheat/*Puccinia graminis*	S	Reduced disease development.	No effect.	26
Corn/*Helminthosporium maydis*	S	Reduced disease development.	-	26
Bean/southern bean mosaic virus	S	Increased virus titer.	Increased sulfur uptake.	27

continued...

Table 25 (Continued).

Plant/Pathogen	Exposure[1]	Effect on Pathogen Induced Disease	Effect on Pollutant Injury on the Plant	Ref.
SULPHUR DIOXIDE				
Corn/maize dwarf mosaic virus	S	Increased virus titer. Increased symptom severity.	No effect.	27
Tomato/tobacco mosaic virus	S	No effect.	No effect.	27
Corn/*Corynebacterium nebraskense*	S	Reduced and delayed disease development.	No effect.	28
Soybean/Mex. bean beetle	S	Increased beetle fecundity.	-	29
ACIDIC PRECIPITATION				
Corn/*Helminthosporium maydis* (N cytoplasm)	A	Increased disease development.	-	30
Corn/*H. maydis* (N cytoplasm)	A	No effect.	-	30
Corn/*H. maydis*		No effect.	No effect.	31
Kidney bean/*Uromyces phaseoli*	A	Decreased disease development.		30,32
Kidney bean/ *Pseudomonas phaseolicola*	A	Post-exposure inoculation; increased disease development.	-	30,32
Kidney bean/root knot nematode	A	Decreased disease development.	-	30,32
Soybean and kidney bean/*Rhizobium* sp.	A	Decreased nodulation.	-	32
Phaseolus vulgaris/ *Meloidogyne hapla*	-	No effect.	No effect.	31
Phaseolus vulgaris/ *Uromyces phaseoli*	-	Inhibited growth.	No effect.	31
Phaseolus vulgaris/ *Pseudomonas phaseolicola*	-	Inhibited growth.	Increased injury.	31

[1] F = Field exposure
S = Sub-acute exposure
A = Exposure causing acute injury
F(A) = Field exposure with acute injury
- = Information not available

continued...

Table 25 (Concluded).

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27. Laurence et al. (1979b)
28. Laurence (unpublished data)
29. Hughes et al. (1983)
30. Shriner (1977)
31. Shriner (1980)

Adapted from Laurence (1981)

Table 26. Simulated acid rain-fungal life cycle interaction (Torn et al. 1987).

Stage	Process	Effect of Low pH
Spore dissemination	Dissemination by water splash	Germination inhibited
Spore on tissue	Spore germinates and grows prior to penetration	Growth stimulated or inhibited
Penetration	Penetration through cuticle stomata or wounded tissue	Wounded tissue increase, stomata close, cuticle eroded
Colonization	Pathogen dependent on host metabolism	Changes in primary and secondary metabolites

References: 1. Shriner and Cowling (1980)
2. Laurence et al. (1983)

et al. (1982) also found that female beetles preferred to feed on sulphur dioxide fumigated young plants first, unfumigated mature plants next, and unfumigated young plants last. He suggested that sulphur dioxide may induce physiological changes in young plants similar to those which occur in older plants and as a result, a shift in the preference of the beetles. The overall result of sulphur dioxide fumigation may be an extension in the period of vulnerability of plants to predation because under normal conditions, the insects feed primarily on older mature plants. Similar types of insect-plant relationships may also occur with other plant species and pollutants.

3.10 ACIDIC DEPOSITION EFFECTS ON AGRICULTURE: LITERATURE CITED

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4. NUMERICAL MODELS OF AIR POLLUTANT EXPOSURE AND VEGETATION RESPONSE

The following section deals with various types of models that attempt to define and predict the effects of air pollutant exposure on plants. Most of these models use dose-response relationships to define and predict effects. Descriptions of the various models may be found in Krupa and Kickert (1987).

4.1 TYPES OF MODELS

A model can be described as information, data, principles and the like, arranged or grouped, usually mathematically, so as to represent or describe a certain idea or condition. Models of biological systems are generally grouped into one of two types (Woodmansee 1974):

a. Statistical or empirical models are composed of mathematical equations that have been statistically derived from sets of data collected in the field or laboratory. These types of models describe the statistical relationships between the dependent variable and one or more independent variables.

b. Mechanistic or process models attempt to represent a biological system in terms of basic, well defined laws or relationships.

Both types of models have advantages and limitations. Statistical models are relatively simple, have easily accessible input requirements and have precision in their output but they have low realism, scientific value, and general applicability to locations other than those in which they were developed. Conversely, mechanistic models are more realistic and are of scientific value but they are usually complex, have difficult to acquire input requirements, and have low precision in their output.

In evaluating the impacts of air pollutants on cultivated and natural vegetation, a number of investigators have proposed statistical models (Larsen and Heck 1976; Benson et al. 1982; Heck et al. 1982; Loehman and Wilkinson 1983; Medeiros et al. 1983; Nosal 1983, 1984; Fox et al. 1986). Others have developed mechanistic models (Ares 1979; Andersson et al. 1980; Haines and Waide 1980; Kercher 1980; Luxmoore 1980; West et al. 1980; Coughenour 1981; Heasley et al. 1981; Kercher and Axelrod 1981; Miller et al. 1982; Harwell and Weinstein 1983; King et al. 1983; Mortensen 1984). These and other similar models have attempted to explain the relationships between acute or chronic pollutant exposures and vegetation responses.

4.2 ACUTE VERSUS CHRONIC EXPOSURE

In the present context, "acute exposure" is defined as the occurrence of short-term (hours to days) high pollutant concentrations. Chronic exposure is defined as the occurrence of long-term (weeks, months, entire life cycle) low pollutant concentrations with periodic intermittent "episodes" or peaks. Generally, acute exposures cause symptoms of injury from which the plant may or may not recover depending on the timing and magnitude of the stress. On the other hand, chronic exposures may or may not cause visible symptoms of injury; however, chronic effects can result in changes in the growth, reproduction, productivity, and quality of the plants.

4.3 CHARACTERISTICS OF AMBIENT AIR QUALITY

When creating a numerical model to describe vegetation responses to air pollutant exposure "understanding of the nature of the cause is as important as understanding the nature of the receptor response" and "sound integration of the two aspects is critical" (Krupa and Kickert 1987). Unfortunately, authors of many models have oversimplified the nature of ambient air quality and therefore the results of their models are of questionable value. Development of models with good predictive capabilities requires that the authors correctly describe the ambient (real world) air quality.

In evaluating the effects of pollutants under real world conditions, one must define the spatial and temporal variability in the pollutant concentrations. For example, high concentrations of ozone (O_3) are generally observed during the daylight hours, while high concentrations of fine particulate sulphate (SO_4^{2-}) are observed during night-time hours (Stevens et al. 1978). This temporal variability in the patterns of the two pollutants has been shown to be of importance in vegetation effects. Fine particulate sulphate (SO_4^{2-}) alone did not produce visible injury, but when plants were exposed to fine particulate sulphate (SO_4^{2-}) followed by ozone (O_3) more than additive visible O_3-type injury was observed (Herzfeld 1982; Chevone et al. 1986).

In addressing this issue one must also correctly provide an appropriate numerical description of the frequency distribution of the pollutant concentrations and exposure over time. Many scientists assume that, for the purposes of their models, the frequency distribution of pollutant concentration follows a normal, "bell-shaped" distribution (e.g., Oshima et al. 1976; Male 1982; and Heagle et al. 1986). In reality it has been shown that the frequency distribution of the occurrence of oxides of nitrogen (Pratt et al. 1983), sulphur dioxide (Berger et al. 1982; Fowler and Cape 1982; and Buttazzoni et al. 1986) and ozone (Lefohn and Benedict 1982; Nosal 1984) are all skewed toward low concentrations, with a long tail toward high values. Several mathematically derived theoretical distributions have been proposed to describe the nature of the observed pollutant frequency distributions, for example, the log-normal distribution (Fowler and Cape 1982; Male 1982) and the two parameter gamma distribution (Berger et al. 1982). However, most recently the Weibull distribution has been proposed as a universal form for the interpretation of air quality data (Krupa and Kickert, 1987) because the log-normal distribution does not possess the characteristics to sufficiently explain the generality or universality and the gamma distribution is computationally inconvenient.

In addition to the previously discussed gaseous pollutants (ozone and oxides of nitrogen and sulphur) the phenomenon of acidic rain is of substantial concern. Almost all studies of acidic rain relate to the use of "simulated rain." This involves treating plants with a "solution of constant chemical composition, applied artificially at constant or varying amounts." However, in the real world the chemistry of precipitation varies significantly within and between individual rain events (Pratt et al. 1983). This fact questions the results of the "simulated rain" experiments and the models derived from the results of such experiments. The experiments normally use "average" values of the constituents in precipitation to develop the "simulated rain." The use of average values and linear statistical regression techniques are inappropriate because the data invariably violate the statistical assumptions of normality, homoscedasticity, unbiased residuals, and independence (Nosal and Krupa 1986). In addition, there are a

number of other concerns introduced through artifacts caused by sampling methodology (Electric Power Research Institute 1986), the duration of the sample collection period (Sisterson et al. 1985), the methods used in data analysis (Krupa and Kickert 1987), and the seasonality of data collection.

Finally, Krupa and Kickert (1987) raised concerns that little if any effort has been made to adequately describe the statistical distributions of the fine particles which contain a major portion of sulphate and nitrate.

4.4 THE CONCEPT OF POLLUTANT DOSE

Pollutant dose can be defined as the exact amount of a given pollutant to which a given receptor (plant) is subjected at one time, or at staged intervals. Historically, dose has been expressed as:

1. Pollutant concentration multiplied by the duration of the exposure;
2. Pollutant concentration divided by the duration of the exposure; or,
3. The sum of the concentration multiplied by the duration of the exposure, when the pollutant concentration exceeds a set minimum threshold (integrated exposure: Lefohn and Benedict 1982).

The pollutant dose "indices" have several drawbacks. They assume a normal distribution of ambient pollutant concentrations. The negative consequences of this assumption are illustrated by the work of Hogsett et al. (1985). Further problems with pollutant averaging techniques have been pointed out by Krupa and Gardner (in preparation). They found that hourly averages of sulphur dioxide concentration, downwind of a large point source in Minnesota, were reported to be zero during 90% of the ten year monitoring period. However, when the continuous data were examined, within the 90% of the time numerous instances of sulphur dioxide concentrations of 0.50 ppm or higher were observed.

The matter is further confounded by the fact that exposure to low concentrations of pollutant can either predispose plants to injury from subsequent episodes or can confer tolerance (Godzik and Krupa 1982). In addition, the developmental stage of the plant during the time of exposure can have a marked effect on its response to a pollutant dose (Lockwood et al. 1977; Teng and Gaunt 1980; and Benson et al. 1982). Finally, atmospheric factors (light, temperature, relative humidity, and carbon dioxide), edaphic factors (moisture and nutrient availability) and other biological factors (specific genetics of the plant cultivar and the presence of pests and pathogens) influence the growth and development of the plant and further confound attempts to determine the response of the plant to the pollutant exposure.

In the context of air pollutant exposure and plant response a satisfactory numerical expression of dose should at least consider:

1. the artifacts of pollutant averaging techniques;
2. the episodicity of pollutant occurrence and exposure;
3. the time intervals between episodes; and,
4. the relationship between the pollutant stress and the growth stage of the plant.

Nosal (1983) provided a mixed, multivariate, polynomial, Fourier regression model which accounts for the number of pollutant episodes, the highest peak in pollutant concentration, and the cumulative numerical integral (concentration over time) of exposure. However, the model does not provide a complete numerical explanation of the importance of the individual pollutant episodes or the relationship of exposure to the growth stage of the plant.

A final aspect of dose that has not been addressed by any models relates to "exposure dose" versus "effective dose" (Runeckles 1974). Exposure dose is the pollutant regime to which the plant is exposed. Effective dose is the actual quantity of the pollutant which is absorbed by the plant. No field techniques are currently available to measure effective dose, although the use of radioactive tracers or the computational approach of pollutant absorbed dose (PAD) suggested by Fowler and Cape (1982) offer possibilities. [PAD = mean pollutant concentration multiplied by exposure time multiplied by canopy conductance.]

4.5 MATHEMATICAL MODELS FOR CHARACTERIZING PLANT RESPONSE TO AIR POLLUTANT STRESS

Krupa and Kickert (1987) provide a tabular summary of their review of 30 mathematical models for characterizing plant response to air pollutant stress. This tabular summary provides basic information on the pollutants and receptors considered by the models, a brief statement of the major biological paradigm involved in each case, and the results obtained through the application of each model. In addition, a statement of the advantages, limitations, applicability, and possible modifications for each model is provided. Table 27 provides a summary of the models reviewed by Krupa and Kickert (1987).

4.5.1 Acute Pollutant Exposure and Plant Response Models

Of the 30 models summarized in the review only 6 describe acute pollutant exposure and plant response. Three of these are statistical (empirical) models and three are mechanistic (process oriented) models. The three statistical models are designed to describe the effects of pollutants on agricultural crops. These models are suitable only for preliminary assessment of plant response or preliminary guideline preparation. Of the three process oriented models of acute effects, one is suitable for research only, one requires further development, and one has inadequate documentation.

4.5.2 Chronic Pollutant Exposure and Plant Response Models

The remaining 24 models reviewed by Krupa and Kickert deal with the effects of chronic exposure of pollutants. Most of the statistical models are also only suitable for preliminary assessment of yield loss or preliminary guideline preparation (Table 28). The models of Nosal (1983, 1984) are suitable for environmental assessments if a suitable data base is available. The mechanistic models of response to chronic exposure are primarily suitable for research only. Many of them suffer from inadequate documentation. The models of King (1986) and Mortensen (1984) could be used as preliminary guidelines to develop further research programs for the chronic effects of pollutants on agricultural crops.

Table 27. Summary of the assessment of applicability of the statistical (empirical) models reviewed by Krupa and Kickert (1987).

Model Type	Applicability: Environmental Assessment (if data are available)	Applicability: Preliminary Assessment of Yield Loss	Applicability: Preliminary Guideline Preparation	Applicability: Not Applicable-Indequate Documentation
Acute Effects				
Agricultural Crops			Larsen and Heck (1976) Heck and Tingey (1979)	
Chronic Effects	Nosal (1983)	Benson et al. (1982) Rowe and Chestnut (1985) Heagle et al. (1986) Heck et al. (1984a,b) Heck et al. (1982) Loehman and Wilkinson (1983) Oshima et al. (1976) Medeiros et al. (1983)	Stevens and Hazelton (1976)	
Agricultural Crops				Hazelton (1976)
Natural Plants	Nosal (1984)			Fox et al. (1986) Westman (1979)

Table 28. Summary of the assessment of applicability of the mechanistic (process oriented) models reviewed by Krupa and Kickert (1987).

Model Type	Applicability			
	Preliminary Guideline	Research Only	Requires Further Development	Not Applicable-Inadequate Documentation
Acute Effects				
Agricultural Crops			Kercher (1980)	
Natural Plants				Harwell and Weinstein (1983)
Chronic Effects				
Agricultural Crops	King (1986) Mortensen (1984)	Luxmoore (1980) King et al. (1983) Miller et al. (1982) Kercher et al. (1980) Ares (1979) Andersson et al. (1980) Haines and Wade (1980) West et al. (1980)	Coughenhour (1981)	
Natural Plants				Heasley et al. (1981) Harwell and Weinstein (1983)

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5. EFFECTS OF ACIDIC DEPOSITION ON SOILS

The acidification of soils as a result of acidic deposition and the potential effects on terrestrial ecosystems have been topics of considerable concern in the world in recent years. The potential for, and documentation of, such effects have been focussed in studies on the acidic soils of Scandinavia, northern Europe, northeastern United States, and southeastern Canada. Concern relates primarily to the potential for reductions in forest productivity as a result of acidic deposition and on the potential for acidification of lakes and streams with subsequent reductions in aquatic productivity via soil throughflow and/or overland runoff. More recently, and particularly in Alberta, the potential for adverse agricultural effects which may result from acidic deposition have begun to be addressed.

The following narrative briefly outlines the processes that take place in soils during acidification, the soil buffering systems, and possible mechanisms of the process. The latter part of this discussion will then place these acidifying processes in a world perspective and look at the implications of such effects on soil types in general.

5.1 ACID-BASE SYSTEM IN SOILS

The Bronsted-Lowry concept of acids and bases is commonly applied to soil acids and bases (van Breemen et al. 1983). Soil is composed of many conjugate acid-base pairs. Examples of such acid-base pairs are: $H_3O^+ - H_2O$; $Al(OH)_2^+ - Al(OH)_3$; $H_2CO_3 - HCO_3^-$; and $NH_4^+ - NH_3$.

The strength of acid-base systems in soils is measured by the proton dissociation constant (K_{HA}):

$$HA + H_2O = H_3O^+ + A^-; \quad K_{HA} = (H_3O^+)\,(A^-)/(HA) \qquad [1]$$

$$pH = pK_{HA} + \log\,[(A^-)/(HA)] \qquad [2]$$

When the acid system is strong, the dissociation of protons is increased and the value of K_{HA} is high; the pK for an acid is the pH value at 50% dissociation where $(A^-) = (HA)$.

Soil acidity is best considered in terms of intensity and capacity factors. Capacity factors are a function of the size or quantity of the system and are directly influenced by addition or depletion of protons. Capacity factors are characterized by the amount of base needed to titrate the soil to a set end point. Intensity factors such as pH are a function of the chemical properties of the system and are independent of its quantity (van Breemen et al. 1983). Bache (1980) stated that there are three parameters included in defining soil acidity: the total acidity, the degree or intensity of acidity, and the buffer capacity or the manner in which the degree of acidity varies with total acidity.

5.2 SOIL REACTIONS

The degree of acidity usually represented by pH values is related to the number of free hydrogen ions in solution, which probably exist as the hydrated forms of H_3O^+ and $H_7O_3^+$. However, soils are generally mixtures of porous charged solids and humus with

little solution, which makes it impossible to define theoretically or determine experimentally a unique pH value (Bache et al. 1979a). Measured soil pH values have been found to depend on the following variables as defined by Jackson (1958): drying of the soil, soil-to-water ratio, CO_2 concentration in equilibrium with soil suspension, and solution electrolyte concentration. Because of the variance in soil pH depending on its environmental state, some researchers have suggested alternate methods for its measurement; for example, measurement of the lime potential (Schofield and Taylor 1955; Bache 1979a) or the addition of a standard method of pH measurement made at unique soil-to-water ratios and salt concentrations (Peech 1965).

Currently, soil pH measurements are mainly conducted potentiometrically in dilute electrolyte suspensions. However, such measurements can cause problems because the pH values obtained can vary depending on the position of the calomel electrode in the suspension (Black 1968; Thomas and Hargrove 1984). The suspension effect can be eliminated by suspending the soil in an electrolyte solution ($CaCl_2$ or KCl) of ionic strength greater than 0.005M (Bache 1979a).

Lime potential or the pH of soil measured in a supernatant of 0.01M $CaCl_2$ was proposed by Schofield and Taylor (1955) to circumvent the problems of measurement. They expressed their results as pH-1/2pCa or "lime potential", where pCa is the negative log of the Ca^{2+} activity in solution which is equivalent to the mean activity of $Ca(OH)_2$. Lime potential is considered independent of electrolyte concentration at least for those encountered in soils (Thomas and Hargrove 1984).

In calcareous soils the activities of H^+ and Ca^{2+} are determined by the following reactions:

$$[CO_2]\ soln = k_H\ p\ CO_2 \qquad [3]$$

$$H_2O + [CO_2]soln = H_2CO_3 = [H^+] + [HCO_3^-] = 2[H^+] + [CO_3^{2-}] \qquad [4]$$

$$CaCO_3 = [Ca^{2+}] + [CO_3^{2-}] \qquad [5]$$

The lime potential of soil thus depends on the partial pressure of CO_2 and the temperature of the soil (Talibudeen 1981). In non-calcareous soils, the activities of H^+ and Ca^{2+} ions are determined largely by the following reactions (Thomas and Hargrove 1984; Reuss 1985):

$$Al(OH)_3 + 3\ H^+ = Al^{3+} + 3\ H_2O \qquad [6]$$

$$K_a = (Al^{3+})/(H^+)^3 \qquad [7]$$

$$3\ CaX + 2Al^{3+} = 2\ AlX + 3\ Ca^{2+} \qquad [8]$$

$$K_g = [(AlX)^2 \cdot (Ca^{2+})^3]/[(CaX)^3 \cdot (Al^{3+})^2] \qquad [9]$$

Combining the above equations for K_a and K_g, and rearranging them gives the following:

$$(Ca^{2+})^{1/2}/(H^+) = \frac{[(Ka)^{1/2}K_g^{1/6}(CaX)^{1/2}]}{AlX^{1/3}} \qquad [10]$$

Taking the negative logarithm of both sides gives the following final formula:

$$pH - 1/2\ pCa = K_L \qquad [11]$$

where K_L = lime potential, which is equivalent to the negative logarithm of the right hand side of the equation. This equation 11 states that the lime potential is proportional to the Al H proportionality constant (K_a), the exchange constant (K_g), and the exchange sites occupied by Al and Ca.

The usefulness of the lime potential concept is based on the premise that soil reaction is a product of the interaction and balance of H^+ ions and other mobile ions, whose relationship is best expressed as the H^+ activity relative to the reduced ratio of other cations (Bache 1979a). The other cations include Ca^{2+}, Mg^{2+}, and Na^+ in calcareous soils plus Al^{3+} in acidic soils.

Buffering in soils is chiefly due to colloidal organic and inorganic materials. Buffering capacity may vary with pH and may also be time dependent as dissolution kinetics vary with the composition of the soil. The inorganic colloidal soil complex functions as a slightly ionized acid or as a slightly ionized salt of a weak acid. Clays act as weak acids due to exchangeable aluminum which hydrolyzes and exhibits different forms varying with pH as shown below:

$$\underset{\text{mono-nuclear ions}}{Al^{3+}} \longleftrightarrow Al(OH)^{2+} \longleftrightarrow \underset{\text{poly-nuclear ions}}{Al_n(OH)_m^{(3n-m)+}} \longleftrightarrow Al(OH)_3 \longleftrightarrow \underset{\text{solid}}{Al(OH)_4} \qquad [12]$$

approximate pH: 3.5 — 5 — 6.5 — 8

There are four major soil buffering systems all of which are pH dependent. They are: aluminum buffering (approximately pH 4), iron buffering (pH range less than 3 to 3.5), carbonate buffering (pH range 6.5 to 8.3), and organic buffering (pH range 4.5 to 6.5) (Ulrich 1980).

The basic formulas and reaction types for each type of buffering system are as follows:

Aluminum: $AlOOH \cdot H_2O + xH^+ = Al(OH)_{3-x}^{x+} + xH_2O$ [13]

Iron: $Fe(OH)_3 + xH^+ = Fe(OH)_{3-x}^{x+} + xH_2O$ [14]

Carbonate: $CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$ [15]

Organic: $R - COOH + H_2O = R\text{-}COO^- + H_3O^+$ [16]

In the normal pH range of soils, the organic soil colloids can act as a buffering system. Carboxylic (-COOH) groups are chiefly responsible for acidity in organic soils within the pH range of 3 to 7. Phenolic -OH groups contribute acidity between pH 8 and 12. Between pH 7 and 8, acidity is contributed by both carboxylic and phenolic-OH groups plus x-NH_2 groups (Gessa 1979). The range of the organic buffering system spans all of the above pH values and is therefore active in most soils.

5.3 TOTAL SOIL ACIDITY

Many approaches have been used to characterize the components of total soil acidity (Bohn et al. 1979). Two generally recognized components are exchangeable and non-exchangeable acidity. These are differentiated on the basis of the experimental method used to measure the particular fraction.

Total acidity is defined as the amount of base required to bring the soil to a pre-determined pH value under standardized conditions (Bache 1980). It is the combined total of free H^+ plus the undissociated forms of acidity in the soil (Holowaychuk and Lindsay 1982). It is, therefore, the sum of both exchangeable and non-exchangeable acidity. The titration parameters and methodology used in determining total acidity must be specified for this type of measurement to be useful. Soil titrations are particularly susceptible to experimental variations such as method of stirring, time of treatment, and period between base additions.

Exchangeable acidity is only detectable in soils having a pH value lower than 5.5. In such soils, exchangeable aluminum primarily constitutes the acidity below pH 4, although exchangeable hydrogen contributed by aluminum hydrolysis is also measured by this technique (Bohn et al. 1979; Thomas and Hargrove 1984). Exchangeable acidity, which comprises a portion of the total acidity, is estimated by leaching or extraction of soils with a 1M solution of a neutral salt and titrating the extract with base (Bache 1980).

The difference between total acidity and exchangeable acidity is the non-exchangeable acidity. This form of acidity constitutes the major part of total acidity in soils and exists mainly in undissociated forms (Bache 1979a). There are three main derivations of non-exchangeable acidity: neutralization of hydroxyl-Al polymers at soil surfaces; neutralization of hydrogen ions from organic functional groups; and displacement of adsorbed anions (Bohn et al. 1979). These processes occur mainly within the pH range of 5.5 to 7.0 but can also occur at higher pH values (Bohn et al. 1979).

5.4 CATION EXCHANGE AND SOIL ACIDITY

The negative charges found on the colloidal clay and humus fractions of the soil matrix give rise to the phenomenon of cation exchange. The cation exchange capacity of a soil is composed of a constant permanent charge and a variable pH-dependent charge (Bache 1979b).

The permanent charge is independent of soil pH and is generally constant for the pH range of most soils. This charge is derived from the isomorphic substitution of Al^{3+} for Si^{2+} in the tetrahedral layers, and of Mg^{2+} or Fe^{2+} for Al^{3+} in the octohedral layers of clay-sized layers of silicate (Bache 1979b). The result of such substitution is that hydroxyl and O^{2-} charges in the clays become unbalanced and acquire a net negative charge.

The source of the variable charge in soils is the pH-dependent dissociation of functional groups on the surfaces of soil solids. These groups include the following: hydroxyl, carboxyl, phenolic, and amine in soil humus, and the aluminol and silanol groups on the crystal edges of layer silicates and the surfaces of aluminosilicate gels (Bohn et al. 1979). Variable charges are also derived from blocking of negative charges by adsorbed hydroxyl aluminum cations (Bache 1979b).

5.5 BASE SATURATION

Base saturation is defined as the ratio of basic exchangeable cations to the total cation exchange capacity (CEC) of the soil. These base cations include Ca, Mg, Na, K, and NH_4. The degree of base saturation (BS) is formulated as follows:

$$\text{Base Saturation} = [(Ca + Mg + Na + K + NH_4)/CEC]100 \quad [17]$$

The degree of base saturation is dependent on the pH at which the CEC measurement was made; they are inversely related.

A two step ion exchange process is used to obtain CEC values. In the first step, soil samples are leached with salts to extract exchangeable cations and saturate exchange sites with an indexed cation; in the second step the indexed cation is leached. CEC is then calculated from the total concentration of the indexed cation in the leachate.

There are three main methods of obtaining CEC which vary depending on the starting pH of the soil, and unfortunately, each gives a different value for CEC but the same value for base saturation. Bache (1979b) stated that the relationship between CEC and exchangeable ions can be represented as follows:

$$\text{CEC} = \text{exchangeable base cations} + \text{exchange acidity (acid cations)} + \text{hydrolytic acidity} \quad [18]$$

As the pH of the extracting solution increases, the amount of exchangeable base cations stays constant but CEC increases due to increased acidity. This results in a decrease in base saturation as the pH rises. The strong interdependence of base saturation on pH of the extracting solution used to determine CEC makes base saturation an unreliable measure of soil saturation with base cations or unsaturation with acid cations. The most realistic picture of any losses in base saturation due to acidification should be obtained with measurements taken at the native soil pH.

5.6 NATURAL ACIDIFICATION OF SOILS

5.6.1 Acidification in Soil Genesis

Soils and their composition are considered to be a function of many different factors such as parent material, climate, biota, topography, and time (Jenny 1941). Parent material, topography and time are passive factors in soil development, whereas climate and biological action are considered to be active factors which drive soil processes.

Acidification is an increase in the total acidity of the soil and a reduction in its pH. Over time this process causes a transformation of the chemical conditions of the soil with respect to H^+. Climatic influences on soil acidification result from the effects of temperature and water on the weathering of material and the types and levels of activity of soil biota. Acidic deposition on soils results in bicarbonate weathering as the acid strips $CaCO_3$ from the soil. Other processes that also accompany this acidification are hydrolysis, hydration, and carbonation. These processes cause the decomposition of soil mineral constituents (Tabatabai 1985). Soil acidification is enhanced in high rainfall areas, or as the duration of these acidifying processes increases.

Decomposition of vegetation as a result of biological action in the uppermost soil layers can result in the release of both bases and acids (inorganic and organic). Production of acids is particularly high in the biologically active surface layers of forest soils (i.e., litter zone). In comparison with grassland soils, forests are much less efficient in recycling and retaining nutrients. In part, this is related to the moisture regime of the ecosystem. Grasslands in general are drier and this results in a lower leaching rate and in the retention of the primary buffering cations. Over time, forest soils will become more acidic under natural conditions with acidic deposition causing a possible acceleration of this natural effect. Changes in the pH of the litter layer also directly affect the types of biota living there, and hence, the decomposition processes that occur. This aspect, however, will be discussed in detail in a later section of this overview and is only mentioned here.

5.6.2 Natural Sources of Soil Acidity

There are various sources of hydronium ions responsible for soil acidity. The various sources, sinks, and pathways of soil acidity are shown in Figure 2 (Krug and Frink 1983a).

5.6.2.1 Organic Matter. The organic layer of soils consists of live organisms (plant and animal) and their undecomposed, partly decomposed or transformed remains. Humus is part of this layer and is composed of the transformed remains of vegetation or animal matter. Humus includes humic substances which are differentiated on the basis of pH dependent solubility into fulvic, humic, and humin fractions, and non-humic substances from the following classes: carbohydrates, proteins, lipids, and organic acids (Paul 1970; Oades and Ladd 1977).

In neutral and alkaline soils, most of the organic matter is in the humus form with large proportions in humic and humin fractions. These materials have high concentrations of carboxyl, phenol hydroxyl, and other functional groups which dissociate to produce hydrogen ions. These groups weather and decompose soil minerals by complexing with and dissolving metals. Calcium is selectively adsorbed by humus material and the Ca-humic complexes may counteract acidification (Wiklander 1979). In acidic soils, humic and fulvic acids are present mainly as iron and aluminum complexes (Thomas and Hargrove 1984). With the gradual decomposition of organic matter in such soils, Al and Fe are released and can contribute to overall acidity by hydrolysis. However, in acidic soils most of the acid produced is lost from the system as H_2O or CO_2 following

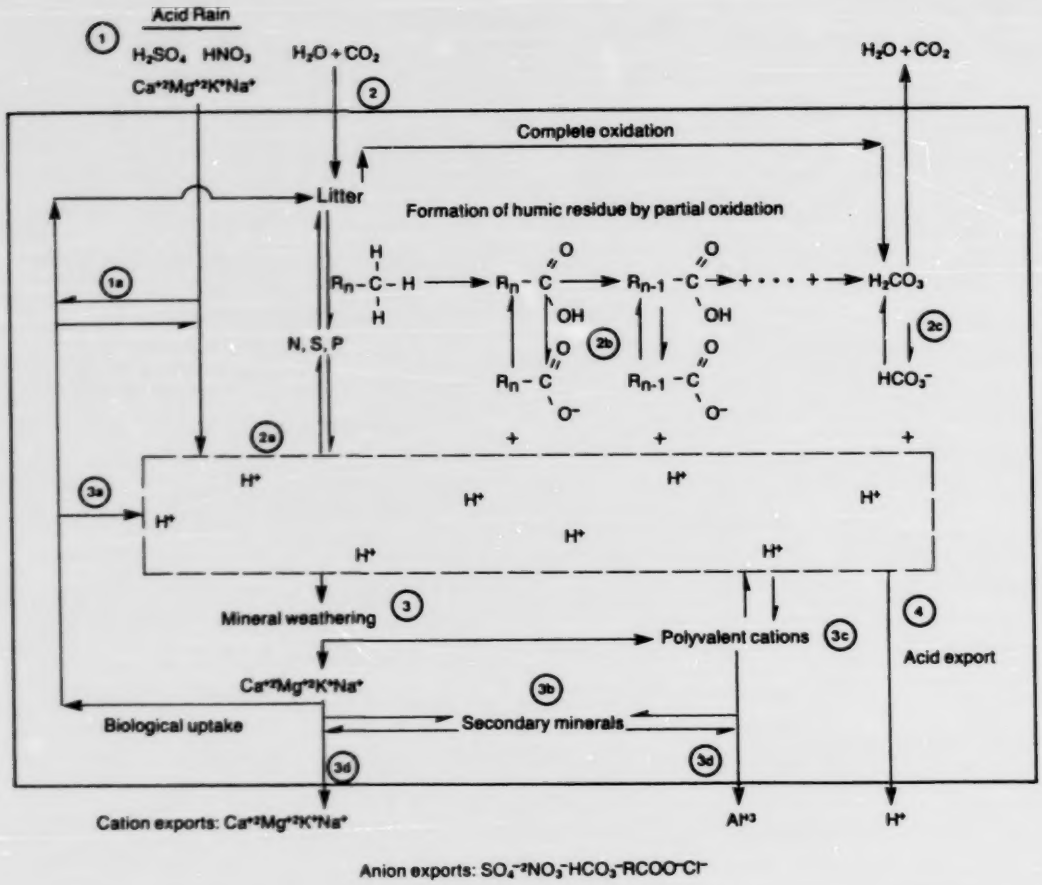

Figure 2. Major sources and sinks of acidity in soil (Source: Krug and Frink 1983a).

Acid rain (1) is a source of acidity, and its composition may be altered before reaching the soil (1a). Although biological processes (2) are net sources of acidity, this obscures the fact that they serve as a substantial sink in acid soils through production of weak organic acids (2b) with ultimate conversion to CO_2 and H_2O (2c). Mineral acids (2a) can be cycled rather tightly with some S and N lost to the atmosphere by microbial activity, and some S and P can be converted to essentially insoluble secondary minerals. Weathering of minerals (3) generally consumes acid in excess of cation export (3d), as secondary minerals (3b) and hydrolysis products of aluminum, iron, manganese (3c) accumulate in soil. Aggrading vegetation causes net cation uptake (3a), and contributes to acidification. Rain less acidic than the soil solution promotes acidification by hydrolysis (3c). The electrical charges exported by cations (3d) and acids (4) are balanced principally by anions shown at the bottom of the figure.

decomposition, rather than contributing to weathering or being translocated through runoff.

Organic acids can have an acidifying influence on soils. For example, the litter layer in coniferous forests is very acidic and produces an acidic humus. The soluble organic substances, including fulvic acids of this soil horizon, are leached and cause strong acidification and weathering which eventually lead to the formation of podzols with low base saturation (Wiklander 1979). Podzol A horizons are developed by leaching while illuvial B horizons result from accumulation of Fe, Al, and humic materials. Bases do not moderate the acidifying influence of this process primarily because they are maintained in the humus layer by biological cycling and do not leach out.

Litter from deciduous hardwood forests is higher in base content than that of coniferous forests. Consequently, hardwood litter tends to increase the alkalinity and the overall buffering capacity of the humus layer, thus making it more resistant to acidifying processes. Grasses are even more effective than trees in reducing acidification since they maintain high base contents and resist leaching of the major nutrient salts by having highly efficient recycling capabilities (Tabatabai 1985).

Ammonium represents another source of potential acidity in soils. There are three primary sources for ammonium in soils: decomposition of vegetational matter by soil microbes; fertilizer applications; and atmospheric deposition. In soils, the ammonium ions are microbially oxidized to form nitric acid. Theoretically, 1 mole of ammonium would produce 2 moles of hydrogen ions following nitrification. In practice, however, direct uptake by plants, volatilization, denitrification processes, and the high ratio of nitrogen uptake to excess base uptake by plants reduces the net effect on soil acidity caused by ammonium additions.

The oxidation of sulphur compounds such as S, FeS, FeS_2, and H_2S also generates acidity. Sulphur, in the sulphate form, is taken up by plants and incorporated into plant materials in its various reduced organic forms. Because of this action, although the original oxidation of sulphur compounds generates soil acidity, no net change in acidity occurs as the sulphur goes through this reduction cycle (Holowaychuk and Lindsay 1982).

In anaerobic soils, sulphate is reduced to sulphide, leading to H_2S or FeS_2 (pyrite). If these soils then become aerobic, acidity is produced by oxidation. Highly acidic soils with pH values as low as 2 have been created by this type of process in, for example, floodplain areas (Thomas and Hargrove 1984). Conversely, waterlogging or flooding of soils leading to anaerobic conditions can reverse this process, thereby counteracting the acidification process (Wiklander 1979).

Nutrient uptake by plants can also have a significant effect on soil acidity. Cation exchange, whereby nutrient cations are adsorbed by root surfaces, causes the desorption of hydrogen ions by the root, resulting in base cation replacement in the soil and a net change in soil acidity. Wiklander (1979) stated that this action likely causes a depressive effect on base saturation in fertile and cultivated soils but found the exact magnitude of change difficult to quantify. The form of nitrogen taken up by plants was also found by Ulrich (1980) to have a bearing on soil acidity. If, for

example, nitrogen was taken up as NO_3^- no acidity was produced, but if nitrogen was taken up as NH_4^+, up to 4 kmol (H^+) ha^{-1} y^{-1} could be produced.

In summary, the above discussion indicates that soil acidification is a natural process which produces an excess of H^+ over time. The mechanisms and intensity of acidification are dependent on the soil forming processes. Table 29, adapted from van Breeman et al. (1983, 1984) summarizes the hydrogen ion producing and consuming processes in soils.

5.6.2.2 Leaching and Weathering. Leaching is the downward movement of dissolved substances through soils as a result of water movement. Substances prone to leaching include soluble salts, bases, silicon, and various forms of organic material. Leaching mechanisms involve many variables such as the nature of the soil medium, activities of microorganisms, formation of complex ions, surface charge and exchange properties of soil particles, partial pressure of CO_2, and porosity and hydraulic conductivity of the soil (Finkl 1979). The degree and type of leaching differs under acid, neutral, and alkaline conditions and under oxidizing versus reducing conditions.

The effect of leaching on soil chemistry varies according to the substances being acted upon. Readily soluble substances such as salts usually percolate with water from upper to lower soil horizons. On the other hand, the alkali and alkaline elements either in mineral or exchangeable form are mobilized by hydrolysis by dilute acids such as carbonic acid. The kind and extent of mobilization is governed by exchange reactions with cations in the percolating waters (Holowaychuk and Lindsay 1982). The bonding energy of cations on exchange sites and in soil solution influences the extent to which different cations are displaced or adsorbed. At a pH of 5.5 or higher, hydrogen ions have high bonding energy and are very efficient in displacing bases.

Weathering is accelerated under high leaching rates. In addition to mobilization of alkali and alkaline earth elements during hydrolysis, silicon can also be released and leached, mainly as silicic acid. Because leaching reduces the concentration of soluble weathering products, conditions conducive to the continuation of weathering are produced. These processes not only contribute to loss of bases but, in the case of primary aluminosilicate minerals, to an increase in the aluminum content of the weathering residues (Holowaychuk and Lindsay 1982). Aluminum and iron form complexes and chelates with acid radicals or functional groups of humic materials. In these forms, iron and aluminum are subject to leaching but not to as large a degree as the alkali and alkaline earth elements or silicon. The net result of these processes is that bases are depleted from soils, and acidity is increased due to higher proportions of hydronium ions and aluminum and to an accompanying decrease in base saturation of the exchange complex.

In acidic soils, the soil solution tends to be enriched with carbon dioxide and humic materials. The alkali and alkaline earth elements are readily leached, while humus and silicon are leached to a lesser degree. Iron and aluminum, however, are removed in small amounts. In neutral soils, the alkali and alkaline earth elements are also leached but tend to be deposited in deeper horizons as carbonates and sulphates. Leaching of aluminum, iron, silicon, and humus is negligible in neutral soils. In alkaline soils, leaching is restricted because these types of soils mainly occur in arid

Table 29. Summary of proton producing and consuming processes.[1]

Proton-producing processes	Example	Proton-consuming processes
(1) Atmospheric input	H^+ (aq(rain/drain water)) = H^+ (aq(soil solution))	(1) Drainage
(2) Assimilation of cations	$M^+ + R_{OH} = R_{OM} + H^+$ $M^+ + H{\cdot}Ligand = M{\cdot}Ligand + H^+$ $NH_4^+ + R{\cdot}OH = R{\cdot}NH_2 + H_2O + H^+$	(2) Mineralization of cations
(3) Mineralization of anions	$R{\cdot}H_2PO_4 + H_2O = R{\cdot}OH + H_2PO_4^- + H^+$ $R{\cdot}SO_4 + 2H_2O = R{\cdot}(OH)_2 + SO_4^{2-} + 2H^+$ $R{\cdot}NO_3 + H_2O = R{\cdot}OH + NO_3^- + H^+$ $R{\cdot}NH_2 + 2O_2 = R{\cdot}OH + NO_3^- + H^+$ $R{\cdot}SH + 3/2\ H_2O + 7/4\ O_2 = R{\cdot}OH + SO_4^{2-} + 2H^+$	(3) Assimilation of anions
(4) Dissociation of acids	$H_2O = OH^- + H^+$ $CO_2 + H_2O = HCO_3^- + H^+$ $R{\cdot}OH = R{\cdot}O^- + H^+$ $H_n{\cdot}Anion\ (aq) = Anion^{n-}\ (aq) + nH^+$	(4) Protonation of anions
(5) Oxidations	$H_2S + 2O_2 = SO_4^{2-} + 2H^+$ $SO_2 + 1/2\ O_2 + H_2O = SO_4^{2-} + 2H^+$ $NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+$ $NOx + 1/4\ (5-2x)O_2 + 1/2\ H_2O = NO_3^- + H^+$ $N_2 + 5/2\ O_2 + H_2O = 2NO_3^- + 2H^+$ $Fe^{2+} + 1/4\ O_2 + 5/2\ H_2O = Fe(OH)_3 + 2H^+$ $FeS + 9/2\ O_2 + 5/2\ H_2O = Fe(OH)_3 + SO_4^{2-} + 2H^+$ $FeS_2 + 15/4\ O_2 + 7/2\ H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+$	(5) Reductions
(6) Reverse weathering of cations	$M^{n+}\ (aq) + 1/2nH_2O = 1/2nM_2/nO(s) + nH^+\ (aq)$	(6) Weathering of metal oxide components
(7) Weathering of anionic components	$^*NO_{(m+n)}(S) + mH_2O = NO_{(2m+n)}^{2m-} + 2mH^+(aq)$ $Ca(H_2PO_4)_2 = CaHPO_4 + H_2PO_4^- + H^+$	(7) Reverse weathering of anions
(8) Cation/hydronium exchange	$M^{n+} + nH{\cdot}Exch = M{\cdot}Exch + nH^+$	(8) Hydronium/cation exchange
(9) Anion exchange (desorption)	$SO_4{\cdot}\ Exch + 2H_2O = Exch{\cdot}(OH)_2 + SO_4^{2-} + 2H^+$	(9) Anion adsorption

[1] Adapted from the original tables in van Breeman et al. (1983, 1984)

regions. The effects of leaching on acidification are thus greatest in those soils which are already acidic, and it would appear that any additional acidic inputs would accelerate acidification and leaching of base ions.

5.7 INFLUENCES OF SOIL ACIDITY AND ACIDIFICATION ON SOIL PROPERTIES

5.7.1 Organic Matter

The physical and chemical forms of organic matter differ among soils and, as a result, a number of organic horizons are widely recognized (Buol et al. 1980). For the purposes of this discussion, the following broad classifications are recognized:

1. organic matter of Chernozemic soils and surface layers of cultivated soils; along with the melanic organo-mineral horizons of deciduous forest soils, this type is commonly referred to as mull;
2. the L-F-H layers, in different combinations, of forest soils; this type is equivalent to mor as described by Buol et al. (1980);
3. organic matter of Solonetzic B horizons, which occurs as dark coatings on the surfaces of peds;
4. organic matter of Podzolic B horizons occurring as dark reddish brown to black, soft, weakly granular layers;
5. organic matter of Organic soils, or peat, which can occur in various degrees of decomposition.

The organic fraction of soils accounts for the major portion of pH dependent CEC (Bache 1976), and from 25% to 90% of the total CEC of surface horizons of mineral soils (Stevenson 1982). The relationship of CEC to pH for various organic soil types is shown in Figure 3. From this graph it can be seen that CEC and pH are directly related and that a decrease in one results in a decrease in the other. The CEC-pH relationship varies, however, according to the type of organic soil. For example, Figure 3 shows that the CEC of organic soils is much more strongly influenced by pH than CEC of clay. The negative charges associated with humus are also dependent on pH. The covalently bonded hydrogen of carboxyl and phenol groups is not dissociated at low pH values. Hydrogen dissociation occurs with increasing pH, and negative charges on the colloids develop as a result. For these reasons, the amount of humus in a soil, even if only in a small proportion, can significantly contribute to the total CEC value. Many of the exchange sites of organic matter in mineral soils may be blocked because of the formation of organo-clay and organo-metal complexes. The acidification of soil would have the effect of reducing effective CEC and displacing base cations which may then be removed by leaching. One possible remedy to this problem would be to lime the soil, which would effectively increase the CEC by disrupting the organo-mineral complexes and by causing the dissociation of carboxyl and phenolic groups (Stevenson 1982).

Low soil pH (<4.0) has been reported by Jenkinson (1981) to decrease the rate of organic decomposition of rye grass. This decrease was thought to be caused by a decrease in the numbers of microbial species capable of functioning at low pH values. The acid tolerance of fungal species responsible for decomposition in forest litter,

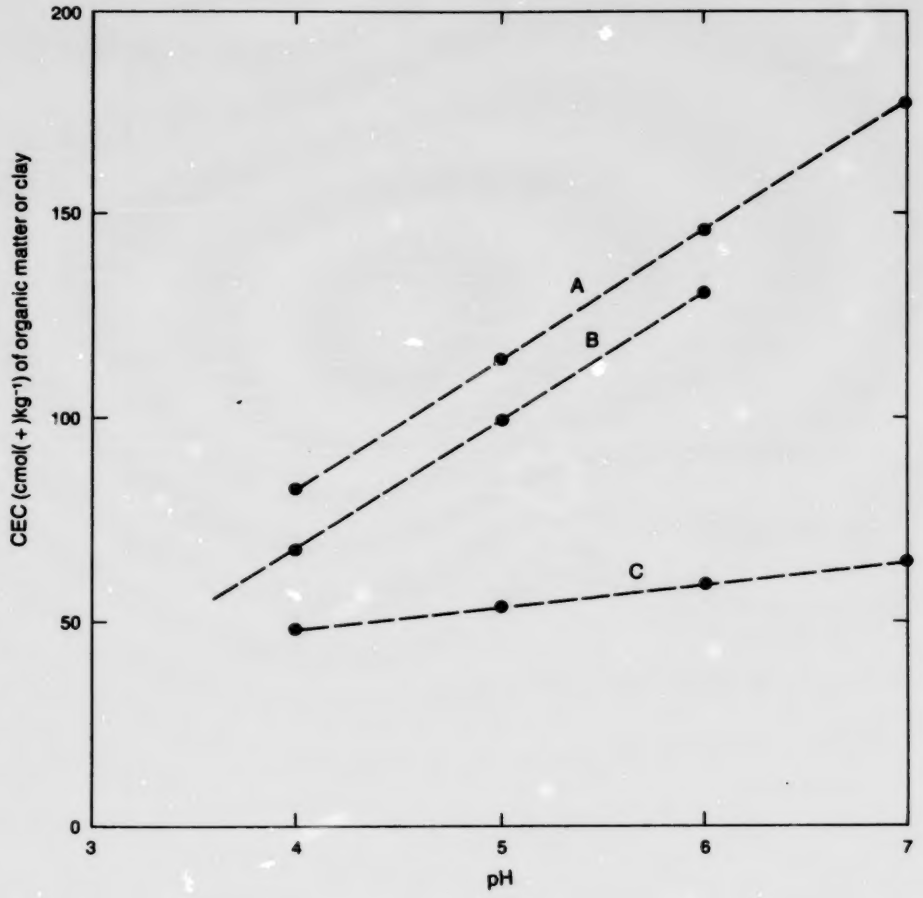

Figure 3. Reduction in cation exchange capacity of organic matter and clay with decrease in soil pH.

A - Organic matter fraction in Ap horizons (Helling et al. 1964)
B - Humus of forest soils (Kalisz and Stone 1980)
C - Clay fraction in Ap horizons (Helling et al. 1964)

makes that system relatively non-responsive to changes in pH although some slight effects are apparent (Abrahamsen et al. 1980). McFee (1982) has listed the suspected results of acidification on organic decomposition as including decreased rates of carbon mineralization as a result of lowered pH or associated heavy metal toxicity, shifts in the microbial community structure away from bacteria towards acid resistant fungal dominated communities, and decreased ammonification and nitrification.

Acidification can also be caused by application of industrial fertilizers. Barratt (1970) found that the soil morphology and humus form was changed as a result of the application of ammonium sulphate fertilizers. In this study, the pH of soils in hay fields dropped (pH 4.5 to 3.9) and the organic horizons of the soil developed the properties of a mor soil. These changes were accompanied by a reduction in decomposition rates and most notably, earthworm activity. Other types of fertilizers did not have these effects on increased acidity, and mull morphology was maintained. In another study, Goh et al. (1986) reported on the physico-chemical effects of the long-term use of urea and ammonium based fertilizers on a Black Chernozemic soil in Alberta. The main effects detected by this study were that the soil exhibited a lowered pH, altered balance among Al and basic cations, exchangeable acidity, and titratable acidity. Although Goh et al. (1986) found that the organic content of the soil increased with fertilization, examination of its microstructure indicated that deterioration had occurred, probably as a result of aggregation.

Schnitzer (1980), in his review on the effects of low pH on the chemical structure and reactions of humic substances, indicated that under moderately acidic conditions, fulvic acids are soluble and mobile while humic acids become aggregated and immobile. These differences in reaction characteristics are thought to be caused by the structural configuration of humic acids. Humic acids are thought to exist as randomly coiled polymers in solution and are most tightly coiled and cross-linked in the centre (Stevenson 1982). Saturation with protons or polyvalent cations, or dispersal in high electrolyte solutions causes the coil structure of humic acids to shrink. Shrinkage is caused by association of ionizable groups and cross-linking of polymers through interaction of functional groups and polyvalent cations. In acidic soils, the most important species causing humic acids to undergo structural shrinkage is Al^{3+}, while in neutral or alkaline soils Ca^{2+} is the dominant agent. This cross-linkage results in smaller, more dense and rigid particles which are thought to be more stable and resistant to biological breakdown (Turchenek et al. 1987). This theory has not been substantiated and at present the structural make-up of humic substances in soils is not known. However, the implications are that increased acidity will cause the aforementioned structural changes with the net result being a decrease in the rates of organic decomposition.

In soils where fulvic acids are the major organic component, such as Podzols, acidification can result in the loss of organic matter due to solubilization and leaching (Schnitzer 1980). Exceptions to this rule occur within the pH range 2 to 3 when fulvic acids may be adsorbed to mineral surfaces, or in clay soils where interlayer adsorption may increase as the clay minerals expand. Increased acidity and fulvic acid leaching result in acceleration of soil weathering which in turn causes a reduction in biological activity and a general lowering of soil productivity (Schnitzer 1980). These effects are extremely rare in soils except under extremely acidic conditions.

The following publications summarize the types of organic matter and mineral interactions and product formation mechanisms under various soil environments, and should be consulted if more detail on this topic is desired: Schnitzer 1978; Burchill et al. 1981; and Stevenson 1982. The role of organic matter and its interactions with soil mineral constituents in aggregation of soils has been reviewed by Tisdall and Oades (1982), and by Oades (1984).

Another effect of increased soil acidity on fulvic acid colloids could be an increased tendency for dispersion and translocation causing the acceleration of the podzolization and lessivage processes. Such induced dispersion may accelerate the development of surface crusts and hard setting properties in certain types of tilled soil. These processes can occur in soils with no free $CaCO_3$ and little solubilized aluminum at a pH of about 6 (Oades 1984). These types of conditions are reasonably prevalent on many of the tilled Luvisolic soils of western and central Alberta (Turchenek et al. 1987).

Clays and organic materials are formed of polyanions which can be bridged by polyvalent cations such as Ca, Mg, Al, and Fe. The minor elements such as Mn, Zn, and Cu also contribute to bridging. The cation bridges can be disrupted by treatment of soil with complexing agents and acids. The effect of such disruption is to cause soil aggregates to become destabilized (Hamblin and Greenland 1977).

Clay-humus interactions can be produced by the introduction of lime which in effect causes the cation bridge mechanism to be activated. The results of such additions have been shown to stabilize soil structure and improve tilth in tilled Luvisols of northeastern Alberta (Hoyt et al. 1981). Thus, in addition to its acid neutralizing ability, lime ($CaCO_3$) also appears to have the ability to reverse the deleterious effects on soil structure that acidification can cause.

5.7.2 Soil Cations and Leaching

The suspected effects of acidification on the soil exchange complex have been summarized by McFee (1982), Mortvedt (1982), and Tabatabai (1985). The effects documented in these references are as follows:

1. decrease in CEC as a result of clay alumination;
2. increase in the CEC of Ultisols as a result of sulphate adsorption;
3. decrease in base saturation and increase in soil acidity; and
4. increased formation of hydroxyl-Al interlayers under acid weathering.

None of these effects purported to be caused by acidic deposition have been demonstrated convincingly (Turchenek et al. 1987). Lack of demonstrable cause-effect relationships is particularly true for agricultural soils.

In a study of beech forest soils in Germany, Ulrich (1980) attributed a reduction in soil pH to wet and dry acidic (H^+) deposition of approximately 1 kmol ha^{-1} y^{-1}. He also noticed a reduction in CEC which was ascribed to an increase in exchangeable Al. Solubilized aluminum as well as exchangeable H^+ and Fe^{3+} also increased (Ulrich 1980). Because the study soil was already acidic (pH 3-4), any increase in acidity would

cause aluminum to solubilize in the form of either Al^{3+} or $Al(OH)^{2+}$ cations. The permanent negative charges on clay minerals found in this type of soil would cause the Al polycations to be adsorbed even in preference to H^+ (Bohn et al. 1979). The adsorbed aluminum and its cations in solution would be in equilibrium but would contribute to soil acidity by means of hydrolysis.

Ross et al. (1985), in studies of a fertilized orchard in British Columbia, found soil effects that mimicked acidic deposition. Their results indicated that concerns regarding Ca and Mg nutrition and possible Al and Mn toxicity with respect to fruit trees and fertilization are warranted. As noted previously, liming can counteract these acidifying effects on soils, a mitigative procedure suggested by Ross et al. (1985).

Although acidification to pH values lower than 3.5 is not likely under natural conditions because of buffering by aluminum hydroxides and mineral weathering which replenishes cations, simulated acidic rain experiments have demonstrated that aluminum can be mobilized (Abrahamsen et al. 1976). Cronan and Schofield (1979) have also shown that aluminum can be leached from forest soils into the aquatic environment under conditions of acidic precipitation. However, it has been suggested by some investigators that high concentrations of solubilized Al in soil and shallow groundwater may be natural and related to climatic factors such as high rainfall rather than acidic deposition (Krug and Frink 1983a,b; Nilsson and Bergkvist 1983).

The influence of acidic deposition on soil cation removal has been the subject of a number of investigations. Some of these have been reviewed by Johnson et al. (1983). Studies of the effects of acidic deposition on the following classes of soils were reviewed: Inceptisols, Ultisols, and Spodosols in Washington, Tennessee, Alaska, and Costa Rica. Base cation losses as a result of acidic atmospheric inputs were considered to be insignificant in each of these studies (Johnson et al. 1983).

Natural cation losses as a result of leaching appear to be increased by: organic acids in cold climates where the soils are undergoing podzolization; carbonic acid in tropical and temperate soils; and nitric acid in nitrogen rich soils such as those with nitrogen fixing vegetation (Turchenek et al. 1987).

A number of mathematical models formulated from similar concepts have been developed to simulate chemical processes in soils that describe the influences of acidic deposition on soil cations (Reuss 1980; Christopherson et al. 1982; Arp 1983; and Gherini et al. 1985). Of these models, one developed by Reuss (1980) utilizes mass balance equations in the simulation and, therefore, seems appropriate to discuss here. His model predicts that a 1:1 removal of bases would occur in non-sulphate sorbing soils under conditions of acidic deposition except in those soils with a very low base saturation. In soils where base depletion was predicted, it was found that as base saturation was depleted calcium removal decreased until the amount leached was in equilibrium with atmospheric input. In arid areas where evapotranspiration exceeds precipitation, the model predicts that the ionic concentration of the soil solution would increase and that the amounts lost via leaching would decrease. Calcium leaching was predicted by the Reuss model to increase with increasing lime potential in soil systems with a high CO_2 partial pressure. The model also predicted a dampening effect on cation loss in sulphate adsorbing soils.

Three limitations of Reuss' (1980) model have been pointed out:

1. only calcium is considered in the model although other cations could be included;
2. the release of cations to the exchange complex by weathering was not considered;
3. the model is strictly abiotic and does not consider plant nutrient uptake.

5.7.3 Soil Anions

Anion sorption properties are important in terms of availability of plant nutrients and for the regulation of the leaching rates of some elements. The general order of affinity of soil for major anions is as follows:

$$H_2PO_4^- > SO_4^{2-} > Cl^- = NO_3^-$$

Nitrate and sulphate are of particular interest since they are both major constituent ions of acidic deposition. Nitrate is not specifically adsorbed and its concentration in the soil solution and its adsorption at a particular pH is governed by pH-charge relationships; that is, little or no sorption occurs above the zero point of charge and sorption increases with decreasing pH. Mott (1981) established that sulphate ions are attracted by hydrous oxide surfaces more than nitrate or chloride ions. Sulphate sorption has been demonstrated experimentally using sulphuric acid leaching, and it was shown that iron podzols have a higher affinity for this ion than semi-podzol or brown earth soils. Sulphate sorption has also been found to be high in iron and aluminum-rich Inceptisols of Costa Rica while the Inceptisols, Utisols, and Spodosols of the United States had a smaller affinity (Johnson et al. 1983).

Wiklander (1981) demonstrated that anions and soil type directly affect the adsorption of cations in soil. For example, the Na, K, Ca, and Mg in association with nitrate and chloride were bound less readily than when in association with phosphate in soils. The same cations had an intermediate affinity for binding when in the presence of sulphate (Wiklander 1980). Polyvalent anions added to soils increase adsorption and decrease leaching of cations through this binding action. Additions of phosphate fertilizers to soils can, therefore, reduce leaching losses of cations, especially if the soils are rich in the hydrous oxides of aluminum and iron (Turchenek et al. 1987).

5.7.4 Availability of Nutrients and Toxic Metals

As part of their review, Turchenek et al. (1987) included a detailed documentation of nutrient cycling as it could be affected by acidic deposition. Since most of their discussion deals with plant and microbial processes, the review synthesis is not included here. The reader is, however, referred to Turchenek et al. (1987) should they wish to cross-link findings from all three major fields of research. Other major reviews of this topic may be found in Mortvedt (1982) and Tabatabai (1985).

5.8 EFFECTS OF ANTHROPOGENIC SOURCES OF ACIDITY

5.8.1 Nitrogenous Fertilizers

The gradual acidification of soils as a result of the nitrification of ammonium based fertilizers has been extensively studied (citations in McCoy and Webster 1977). A review of the reaction chemistry of nitrogenous fertilizers with soils and their components may be found in Penney and Henry (1976). Urea application causes an initial increase in soil pH by forming NH_3 which is then oxidized by the bacterium Nitrosomonas to form NH_4^+ and nitrite (NO_2^-). The oxidation process (NH_3 to NH_4^+) produces 2 moles H^+ per mole of NH_4^+. Nitrite is then converted by Nitrobacter to nitrate (NO_3^-).

Ammonium sulphate has the highest equivalent acidity of the various nitrogen based fertilizers and requires a $CaCO_3$:N ratio of 5.35 for neutralization (Penney and Henry 1976). In comparison, anhydrous ammonia, urea, and ammonium nitrate require a ratio of only 1.80 for neutralization. The actual impact of the acidifying process is determined by a variety of factors such as proportion of fertilizer taken up by plants prior to nitrification, NH_4^+ and NO_3^- concentration, pH of the soil, oxygen supply, and temperature (Alexander 1977). Under field conditions, the fixation and leaching of nitrogenous ions and the influences of these ions and plant growth on base mobilization determine the amount of acidity actually produced. Because of the complexity of the above processes and their interdependence, acidification as a result of nitrogen fertilizer application under field conditions has usually been determined empirically. McCoy (1973) and Penney and Henry (1976) have reviewed this topic.

The problem of acidity in agricultural soils of the Western provinces of Canada and in particular, Alberta, has been reviewed by Penney et al. (1977) and Hoyt et al. (1981). The primary cause of acidification in most instances was fertilizer usage and not industrial emission-caused acidic deposition, although this was cited as another possible cause. Ross et al. (1985) reported the acidification of orchard soils in the Okanagan Valley of British Columbia as a direct result of fertilization. Numerous other studies (McCoy and Webster 1977; Hoyt et al. 1981; and Nyborg and Mahli 1981) have substantiated the effects of fertilization on soil acidity, which include lowering of surface and subsurface pH, aluminum solubilization, and consequent leaching.

Liming of soils seems to prevent the acidification process even when fertilization practices continue. It has been suggested that liming should become a general practice to combat soil acidification (Hoyt et al. 1981). These authors also concluded that, if in general liming is practiced to fight fertilizer caused acidity in soils, it would negate any effects of the deposition of acid forming compounds. Specifically with regard to agricultural soils, Turchenek et al. (1987) felt that SO_2 and NOx would not threaten agricultural productivity if liming practices became general and, in fact, the addition of these plant nutrients via atmospheric deposition may be beneficial. A study conducted by Sauerbeck (1983) in West Germany tends to support the liming hypothesis. His results showed that local S deposition rates at his study sites varied from 20 to 100 kg S ha^{-1} but, as a result of liming, soil acidification did not occur and little damage to field crops resulted. Sauerbeck also found that liming caused cations that normally would have leached from the soils under acidifying conditions to be retained.

5.8.2 Atmospheric Deposition

The main acid forming atmospheric pollutants in Alberta are anthropogenic emissions of SOx, reduced sulphur compounds, and NOx (Hunt et al. 1982). The removal from the atmosphere of these compounds falls into two general categories - wet and dry deposition. The various mechanisms for each type of deposition have been categorized by Fowler (1980), Galloway and Parker (1980), and Krupa et al. (1987), and are as follows:

1. Wet Deposition
   a. Incident wet deposition - gravitational transfer of water to earth surfaces;
   b. Throughfall - water that has passed through a leaf canopy;
   c. Net throughfall - difference between throughfall and incident deposition for a particular area.
2. Dry Deposition
   a. Dry fall - soil and seasalt particles of, for example, >10-30 μm diameter which settle by gravity;
   b. Aerosol impaction - particles of <3 μm diameter which deposit on to surfaces. These are commonly particles of $(NH_4)_2SO_4$, NH_4NO_3, and others;
   c. Gaseous adsorption - gases sorbed by foliage or soils (i.e., SO_2, NOx, and CO_2).

Recent reviews of deposition mechanisms and interactions of gaseous and particulate materials in relation to their effects on plant and soil surfaces have been provided by Fowler (1980), Chamberlain (1986), and Weidensaul and McClenahen (1986).

The resistance concept as reported in Fowler (1980) has been used to mathematically describe the flux of atmospheric deposition to surfaces such as soils. The actual surface resistances of soils have not been measured, however, due to their extremely heterogenous nature. It is known that resistance increases with decreasing soil pH and increasing dryness. More gases will be sorbed by soils with high moisture content or high calcium content since both properties exhibit almost negligible resistance factors. This is true for the major gases and/or vapours SO_2, NO_2, and HNO_3^- (Turchenek et al. 1987). Other gases that can be adsorbed during the deposition process include nitrous oxide, nitric oxide, hydrogen sulphide, methyl mercaptan, dimethyl disulphide, carbonyl sulphide, and carbon disulphide (Committee on the Atmosphere and the Biosphere, U.S. 1981).

Gaseous vapours and particulate materials can be incorporated into cloud droplets with deposition occurring as a precipitation event. The adsorption and oxidation of acid forming gases by cloud and rain droplets has been described by Fowler (1980) and Krupa et al. (1987).

Very little in the way of hard data is available for Alberta with respect to dry deposition. Caiazza et al. (1978) found dry:wet deposition ratios of 4.8 for sulphate and 2.1 for total nitrogen in the Edmonton area. Dry deposition inputs to a mixed hardwood forest in the eastern United States have been found to be much more important than had previously been thought (Lindberg et al. 1986). While wet deposition

was the primary source for SO_4^{2-} and NH_4^+, dry deposition was most important for fine particle or vapour NO_3^- and H^+ and for coarse particle K^+ and Ca^+ .

Generally, soils have a high sulphur sorption capacity and the reactions of atmospherically deposited sulphur with soils have been reviewed extensively by Chaudry et al. (1982) and by others. Sulphur sorption is influenced to a major extent by soil moisture content. Nyborg et al. (1977, 1980) and Hsu and Hodgson (1977) have demonstrated experimentally that Alberta soils have a high capacity for sulphur sorbtion and that this can result in pH depression. In their studies, Nyborg et al. (1977) found increases in sulphur of 12 to 53 kg ha^{-1} downwind of SO_2 sources. The highest sulphur gains in these experiments were at sites close to, or farthest from, the source at a distance of 2 and 37 km. Generally, little of the sorbed sulphur was in the form of sulphate. Evaluation of the other potential sources such as snow pack melt, rainfall, and surface waters indicated that the primary source of sulphur was dry and not wet deposition, although the latter contributed to the overall loading.

The results of the aforementioned studies of SO_2 deposition and acidification were only approximations but do indicate a potential for the acidification of Alberta soils. Some limitations of these studies were pointed out by Turchenek et al. (1987) and are as follows:

1. the method of total S determination in the study was imprecise;
2. pH depressions reported of 0.1 and 0.2 units were within the temporal and normal spatial variability for the type of soil studied;
3. extrapolation errors involved in converting small sample plot data to a kg^{-1} ha^{-1} loading may have been large;
4. the S forms involved were not identified.

In most natural and agricultural ecosystems, air pollutants will first encounter plant canopies. Plant canopies have a tremendous SO_2 sorption capacity which diminishes with the time of exposure. This topic has been discussed at some length in a previous major section of this report. However, in any study of the effects of acidic deposition on soils, vegetation processes must be taken into account in an integrative way for interpreting the data or for precise determinations of impacts. This point was also made by the study group of Turchenek et al. (1987) whose document forms the basis of the soils portion of this report.

5.9 SUMMARY

A summary of the potential impacts of acidic deposition on soils is given in Table 30 which was derived from Turchenek et al. (1987), McFee (1982), and Cook (1983). With respect to agricultural lands, Table 31 shows the estimated amounts of cultivated land in different ranges of soil pH for the Canadian Great Plains (Turchenek et al. 1987).

Table 30. Summary of the potential impact of acidic deposition on soils.

Process or Property	Hypothetical Impact of Acid Deposition
I. Soil Exchange Complex	
Exchange Capacity	Decrease in CEC resulting from clay alumination Increase in CEC of soils with oxy-hydroxides due to sulphate adsorption
Exchangeable Acidity	Increase
Base Saturation	Decrease
Clay Mineral Morphology	Increased formation of hydroxy-Al interlayers and acid weathering
Aluminum	Increased mobilization and leaching Increased availability and toxicity
II. Organic Matter	
Organic Matter Turnover	Decreased rate of C mineralization due to acidification and/or associated trace metal toxicity Decreased CO_2 flux from land to atmosphere Increased retention of organic matter
Microbial Community Dynamics	Shift from bacteria to more acid - tolerant fungi
Organo-Mineral Associations	Reduced organo-clay interaction due to disruption of cation bridge linkages
Root Uptake	Trace metal toxicity due to acidification
III. Plant Nutrients	
Nitrogen	Decreased ammonification Decreased nitrification Changes in products of denitrification Increase in leaching Enhanced cation leaching due to NO_3^- inputs Reduced plant availability

continued...

Table 30. (Concluded).

Process or Property	Hypothetical Impact of Acid Deposition
Sulphur	Increased SO_4^{2-} reduction in low S, anoxic systems Increased reduced-S flux and reduced CH_4 flux to atmosphere Decreased leaching of S Decreased leaching of cations in sesquioxidic soils; increased leaching in others Reduced plant availability
Phosphorus	Decreased leaching and AlPO4 precipitation in soil with high Al Increased PO_4^{3-} solubilization, plant availability and leaching in calcareous soils Reduced availability with pH reduction
Fe, Mn, Zn, Cu, Co	Increased availability Increased leaching
Mo, B	Reduced availability
Ca, Mg, K	Reduced availability Increased leaching
Toxic Elements	Some micronutrients may reach toxic levels due to increased solubility Increased concentrations, toxicity and leaching of heavy metals Increased Al toxicity
IV Weathering	
Carbonates	Increased dissolution
Primary Minerals	Increased dissolution
Clay Minerals	Increased alumination (formation of Al interlayers) Reduced surface charge

Table 31. Estimated amounts of cultivated land in different ranges of soil pH on the Great Plains.[1]

Province or Region	Hectares (x 1000)		
	pH <5.5	pH 5.6-6.0	pH 6.1-6.5
Manitoba		10[2]	
Saskatchewan	202	202	405
Alberta, excluding the Peace River region[3]	230	1166	2276
Peace River region of Alberta and British Columbia[3]	98	447	602
TOTAL	530	1825	3283

[1]Adapted from the original table in Hoyt et al. (1981).
[2]pH <6.0.
[3]Based on soil samples taken during 1962-72.

5.10 EFFECTS OF ACIDIC DEPOSITION ON SOILS: LITERATURE CITED

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6. EFFECTS OF ACIDIC DEPOSITION ON SOIL MICROORGANISMS AND MICROBIALLY MEDIATED PROCESSES.

6.1 INTRODUCTION

The soil microbial community is comprised of six main groups: actinomycetes, algae, bacteria, fungi, protozoa, and micro-invertebrates. The microbial biomass is dominated by the bacteria and fungi, forming 25% and 75% of the total biomass, respectively (Anderson and Domsch 1978). It has been estimated that up to 90% of the respiratory metabolism of the soil-litter system is due to bacterial and fungal activity (Reichle 1977; Persson et al. 1980). For these reasons, much of the research regarding acidic impacts on soil biology has been directed to the bacteria and fungi and their functions.

The major roles of the soil microbial community in maintaining soil fertility have been summarized by Alexander (1980):

1. The transformation of soil nitrogen, phosphorous, and sulphur from organic to inorganic forms, resulting in the availability of these nutrients for utilization by plants;
2. The formation of humus which improves soil structure and promotes root growth due to better aeration and moisture conditions. Soil structure is also improved by the creation of soil aggregates which result from the binding properties of microbial excretions and fungal mycelial production;
3. The decomposition of organic matter and the detoxification of phytotoxins resulting from anaerobic decay processes; and
4. The rapid degradation of toxic substances introduced into the soil including pesticides, herbicides, sewage sludge, and carbon monoxide.

In addition, specialized bacteria and fungi which form symbiotic associations with the roots of many of the higher plants are vital in improving plant nutrition. Examples of such symbiotic organisms are nitrogen-fixing bacteria which form root nodules (Rhizobium) and mycorrhizal fungi which are associated with the roots of 95% of the higher plants and which serve in mobilizing plant nutrients not easily available to root systems.

The effects of acidic deposition on soil microorganisms were speculated to be either acute, resulting from high dosages over short periods, or chronic, resulting from low dosages over long periods of time, i.e., years with periodic, intermittent episodes (Visser et al. 1987).

6.2 GENERAL EFFECTS OF ACIDIC DEPOSITION ON SOIL MICROBES

Acidic deposition may have both direct and indirect effects on soil microbes. Direct effects include:

1. An increase in the hydrogen ion concentration to levels where cell membrane permeability and enzyme systems located at the cell surface are altered. At relatively low pH levels, undissociated acids can enter the cells and affect them by changing the internal cell pH; and

2. The production of soluble anions may or may not be toxic to microorganisms. For example, Babich and Stotzky (1978) tested a number of fungi and bacteria for their sensitivity to bisulphite and sulphite, and observed that the HSO_3^- was more toxic, particularly at pH values below 6.0 where this anion dominated. They argued that since all microbial cells are covered with a thin film of water, the toxic effects of sulphur dioxide could be due to its solubility at high pH and the formation of bisulphite and sulphite on the cell surfaces.

Indirect effects include:

1. An increase in leaching of nutrient cations due to their replacement by hydrogen ions at exchange sites. The resultant nutrient deficiencies may alter microbial growth and reproduction;
2. Increase in solubility of aluminum and iron to levels where they become toxic to microorganisms;
3. A modification in the physiology of plants to a degree where root symbionts become less effective. In addition, changes in chemical and physical properties of the soil as mentioned previously, may adversely influence plant growth with consequential effects on the root symbionts; and
4. A modification of the nutrient quality of plant residues available to the decomposer community. Uptake of sulphur dioxide by the plant, dry deposition of sulphur dioxide on plant surfaces, and enhanced uptake of nutrients such as aluminum and iron due to altered soil chemistry may change the chemical quality of plant residues which may indirectly influence the microbial community.

6.2.1 Influence of Soil Acidity on Microbial Communities

The causes of natural soil acidity have been fully discussed in other sections of this review. The effects of anthropogenic changes to the natural soil acidity have also been reported. In general, the effects of lowered soil pH on the microbial community can be summarized as follows:

1. Soil bacteria, except for S-oxidizing bacteria (*Thiobacillus thioxidans*), and actinomycetes are inhibited below pH 5.0;
2. Fungi show no sensitivity to pH change unless the resultant pH is extremely high or low. In fact, at pH values that inhibit bacterial activity, fungi flourish because of a lack of competition. Protozoans appear to have no marked sensitivity to pH except under conditions that also affect fungi;
3. Blue-green algae are sensitive to pH values below 5.0 while the green algae appear to be less sensitive;

4. All microbially mediated processes, with the exception of S-oxidation, operate optimally at neutral or nearly neutral pH values. Specialized bacteria performing nitrogen fixation and nitrification appear to be sensitive to acidity while fungal processes such as ammonification and decay are not (bacteria performing such processes are, however, sensitive); and
5. Sulphur oxidation appears to be insensitive to soil pH since it can be performed by acid tolerant bacteria and fungi.

A summary of the general effects of soil pH on microbial processes is presented in Table 32.

6.2.2 Summary of Acidic Deposition Effects on Microbial Processes

In their review of the effects of acidic deposition on soil microorganisms, Visser et al. (1987) reviewed a major portion of the current literature on the topic. They concluded that it is difficult to determine if soil acidification caused by acidic deposition has effects on the soil microflora, or the processes they mediate. Most of the studies reviewed by Visser et al. were conducted using simulated acidic rain and showed widely varying effects on the various microbial components of the soil community. The levels at which changes in soil pH begin to affect the various microbial types were summarized as follows:

Nitrogen fixation	pH 6.0
Nitrification	pH 6.0
Ectomycorrhizae	pH not certain
Vesicular-arbuscular mycorrhizae	pH 6.0
Organic decomposition	pH 2-4
Ammonification	pH 3.0
Soil respiration	pH 3.0
Carbon mineralization	pH 3.0
Community structure	pH 3-4
Soil enzymes	pH not certain but possibly 2.0

The majority of studies reviewed by Visser et al. (1987) were conducted on naturally acidic forest soils where microflora adapted to acidity exist. Therefore, these results may be somewhat misleading if one is considering grassland and agricultural systems.

Based on the results of both laboratory and field studies reviewed by Visser et al. (1987), it appears that a pH reduction of naturally acidic forest soils to 3.0 or less would inhibit soil respiration. Due to the high buffering capacity of decaying plant residues and organic matter in the forest floor and the probable adjustment of the microflora previously adapted to acidity to further acidification, acidic rain of at least pH 2.0 or high dosage rates of sulphur dioxide or elemental sulphur would be necessary to reduce the soil pH to an extent sufficient to alter microbial respiration. It is unclear whether or not this would also be the case in agricultural systems.

Table 32. The effect of pH on soil microorganisms[1]

Organism	Effect
Actinomycetes	Low densities at pH<5.0; most abundant at pH 6.5-8.0. Not tolerant of low pH; Streptomyces exhibit poor growth and activity below pH 5.0; in highly acidic environments actinomycetes comprise <1% total viable count. Some acid-tolerant strains do exist.
Algae	Qualitative composition determined by acidity with each individual strain having an optimum pH and a range beyond which organism will not proliferate. Blue-green algae limited to neutral or alkaline conditions; absent below pH 5. Diatoms numerous in calcareous areas. Chlorophyta not as sensitive to pH and are present at wide diversity of pH levels - therefore Chlorophyta dominate algal flora in acid habitats.
Bacteria	Heterotrophic bacteria - optimum pH near neutrality; highly acidic conditions inhibitory. Greater the H^+ concentration, the smaller generally is the size of bacterial community. Soils at pH 3.0 still contain many bacteria. S-oxidizing bacteria - chemoautotrophs, particularly Thiobacillus thioxidans are capable of oxidizing elemental S to SO_4^{2-} and H_2SO_4. Thrive in acidic conditions with optimum growth between pH 2.0 - 3.5.
Fungi	Highly versatile; grow over wide pH range; in culture some have capacity to grow at pH 2.0 - 3.0. Fungi dominate habitats with low pH due to lack of competition from bacteria and actinomycetes for carbonaceous substrates. Individual species may demonstrate intolerance to high H^+ concentrations - may be important to plant pathogens e.g. Plasmodiophora brassicae performs best in acidic habitats while others grow best at neutral pH or higher.
Protozoa	No marked sensitivity to pH; some species in pure culture reproduce at pH 3.5. pH sensitivity is strain specific and some may not tolerate extreme acidity or alkalinity.

[1] Summarized from Alexander (1977).

However, as was discussed in a previous section, acidic deposition tends to cause cation leaching from vegetation which may in fact ameliorate to some extent any acidifying processes by increasing the soil buffering capacity.

Soil litter decomposition appears to be retarded only if plant residues are treated with extremely acidic simulated precipitation (pH 2.0) or fumigated at concentration of sulphur dioxide as high as 530 ppb (Visser et al. 1987). Litter decay does not appear to be affected by acidic precipitation of pH 3.0 to 3.5 based on the results of both field and laboratory studies reviewed by Visser et al. (1987). In studies which did demonstrate reductions in the rate of decay, such effects were observed at a variety of pH values; for example, pH 1.8, and 3.7 to 4.1 for pine, pH 2.9 for spruce needles; and pH 3.7 to 5.0 for birch leaves. In field studies where the input of acidic deposition could not be controlled, reductions of pH from 4.8 to 3.3 or to 3.9 in forest litter layers resulted in an overall increase in litter mass due to retardation of the decomposition process. This suggests that chronic exposures may affect microbial decomposition processes more than acute exposures used in most laboratory studies reviewed by Visser et al. (1987).

The studies performed to date suggest that the activity of most soil enzymes are adversely affected by simulated acidic precipitation but only under conditions of pH 2.0 or less.

Visser et al. (1987) also cited studies which indicated that certain portions of the nitrogen cycle could be adversely affected by acidic deposition. This was found to be particularly true of nitrification and nitrogen fixation which were shown to be inhibited in soils below a pH of 6.0. Bacteria such as Rhizobium would be particularly vulnerable under such conditions.

The effect of acidic deposition on plant-pathogen interactions appears to be small under chronic conditions. Although studies on the effects of acidic emissions on mycorrhizal activity are few, they indicate that these symbiontic relationships are also largely resistant to chronic levels of acidic deposition. Visser et al. (1987) pointed out that most ectomycorrhizal plants are also associated with a diverse array of acid resistant fungi which likely provide a strong defense against environmental change caused by acidic deposition. Certain VA mycorrhizal associations, however, are acid sensitive. Reductions of as little as 0.5 to 1.0 pH unit may render these mycorrhizal associations non-functional, resulting in reduced plant growth.

For additional details the reader is referred to Visser et al. (1987). Many of the studies reviewed were primarily conducted in the laboratory under extremely unreal conditions of acidity and in pure cultures. Only in a few instances were realistic field experiments conducted. As Visser et al. (1987) pointed out, more research is required under field conditions and ambient concentrations to clarify the mechanisms and dosage levels that should be of concern.

6.3 ACIDIC DEPOSITION AND INORGANIC SULPHUR MICROBIOLOGY

The previous section of this report dealt with microbiology as a whole. This section deals solely with inorganic sulphur microbiology based on the review of the subject by Laishley and Bryant (1987).

Sulphur deficiencies in various agricultural soils throughout the world have stimulated interest in soil sulphur systems (Coleman 1966; Wainwright 1978; and Beaton and Soper 1986). Sulphur as sulphate is required by plants for the synthesis of sulphur containing amino acids and eventually protein synthesis. In humid regions of the world, most of the soil sulphur is in the biologically unavailable organic form. Studies by Walker and Adams (1958), Freney (1961), and Tabatabai and Bremner (1972) have shown that organic sulphur represents between 42% and 93% of the total sulphur in many soils in the world. The breakdown of organic sulphur into its biologically useable sulphate form is accomplished by two stages: mineralization of organics; and by transformation of the resulting inorganic sulphur to sulphate. These processes are accomplished by heterotrophic microorganisms which derive their energy from the decomposition of organic matter. If the sulphur content of the substrate is greater than what can be utilized in biosynthesis by the microorganisms, the excess sulphur is made available for other soil processes (Reuss 1975). The global sulphur cycle is shown in Figure 4, showing the key microbial groups responsible for sulphur cycling.

6.3.1 Oxidation Reactions

Inorganic sulphur oxidation and reduction can occur under aerobic or anaerobic conditions and with or without light (Jorgensen 1982). Three major groups of microorganisms are important in the rapid oxidation of soil sulphur. These are as described by Keunen (1975) and Wainwright (1978):

1. The colourless sulphur bacteria of the following families: Thiobacteriaceae, Beggiatoaceae, and Achromatiaceae;
2. Photosynthetic S-bacteria of the Chromatiaceae and Chlorobacteriaceae; and
3. Heterotrophic microorganisms which do not gain energy from the oxidation of sulphur compounds, actinomycetes, bacteria, and fungi.

Wainwright (1978) stated that among these groups, the colourless sulphur bacteria and the heterotrophic microorganisms are the most important in cycling soil sulphur. The photosynthetic bacteria of Group 2 are important in aquatic systems and/or in flooded soils.

Laishley and Bryant (1987) discussed the physiological requirements of colourless sulphur bacteria principally of the genus *Thiobacillus*, its method of obtaining energy from the breakdown of sulphur, and its acid tolerance or sensitivity. The chemical reactions by which various species of the *Thiobacillus* break down sulphur products are shown in Table 33. Laishley and Bryant (1987) also described the environmental requirements of three genera of sulphur bacteria found in hot springs (*Sulfolobus*, *Thiomicrospora*, and *Themothrix*). All of these bacterial groups thrive in areas rich in hydrogen sulphide. The genus *Beggiatoa* also thrives in the presence of high hydrogen sulphide concentrations and has been found in sulphur springs, mid layers of lakes, and in water polluted with sewage (Laishley and Bryant 1987).

The fourth group of bacteria described by Laishley and Bryant (1987) are the phototrophic sulphur bacteria of the Chromatiaceae and Chlorobiaceae. In contrast to plants, these bacteria photosynthesize under anoxic conditions, use hydrogen sulphide as

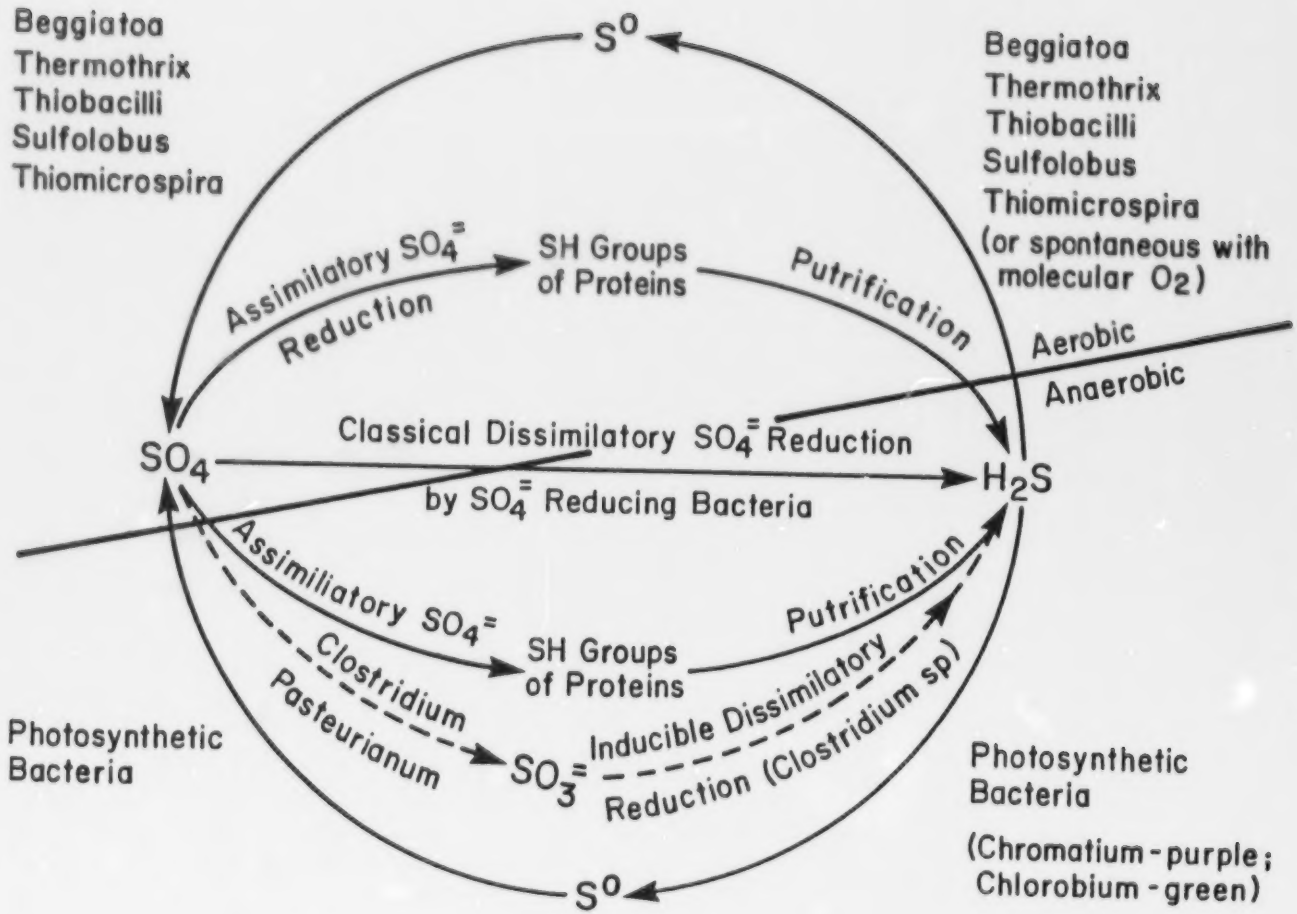

Figure 4. Global sulphur cycle. (Modified after Brock et al. 1984; Laishley 1978; and Laishley et al. 1984)

Table 33. Chemical reactions of the thiobacilli.

(1)	$2S^{\circ} + 3O_2 + 2H_2O$	→	$2H_2SO_4$
(2)	$Na_2S_2O_3 + 2O_2 + H_2O$	→	$Na_2SO_4 + H_2SO_4$
(3)	$2Na_2S_4O_6 + 7O_2 + 6H_2O$	→	$2Na_2SO_4 + 6H_2SO_4$
(4)	$2KSCN + 4O_2 + 4H_2O$	→	$(NH_4)_2SO_4 + K_2SO_4 + 2CO_2$
(5)	$5S + 6KNO_3 + 2H_2O$	→	$3K_2SO_4 + 2H_2SO_4 + 3N_2$
(6)	$5Na_2S_2O_3 + 8NaNO_3 + H_2O$	→	$9Na_2SO_4 + H_2SO_4 + 4N_2$
(7)	$12FeSO_4 + 3O_2 + 6H_2O$	→	$4Fe_2(SO_4) + 4Fe(OH)_3$

Bacterium	Reaction(s) carried out
T. denitrificans	1, 2, 3, 4, 5, 6
T. thioparus	1, 2, 3, 4
T. thiooxidans	1, 2, 3,
T. ferrooxidans	1, 2, 7
T. novellus	2, 3

Source: Starkey (1966).

an electron donor, and produce elemental S, inside or outside the cell. In anaerobic aquatic environments these bacteria oxidize hydrogen sulphide and elemental sulphur to sulphate and in the process derive energy (ATP) required for carbon dioxide fixation. These phototrophic bacteria are mainly restricted to the aquatic systems within a fairly narrow environmental range defined by their requirement for light, hydrogen sulphide, and low oxygen concentrations. These organisms are also further restricted by their tolerance to hydrogen sulphide. Although their importance in sulphur cycling is primarily related to aquatic systems, they are also thought to be of potential importance in flooded soils (Laishley and Bryant 1987).

6.3.2 Heterotrophic Microorganisms

Heterotrophic microorganisms which include bacteria, fungi, and actinomycetes are capable of oxidizing reduced forms of inorganic sulphur. Bacteria such as Arthrobacter, Bacillus, and Flavobacterium oxidize elemental sulphur and bisulphite to sulphate; other species such as Achromobacter sp. and Pseudomonas sp. have been found to oxidize S° and $S_2O_3^{2-}$ to $S_4O_6^{2-}$ (Wainwright 1979). Few reports are available that document the sulphur oxidation properties of fungi and actinomycetes (Wainwright 1979; Germida et al. 1985). Wainwright (1978) found, however, that the fungus Penicillium decumbens was capable of oxidizing elemental sulphur to bisulphite.

6.3.3 Reduction Reactions

Under anaerobic conditions, and at neutral pH, the sulphate reducing bacteria have the unique ability to utilize SO_4^{2-} as an electron acceptor. The process, referred to as dissimilatory sulphate reduction, produces copious amounts of hydrogen sulphide in nature and may also be involved in many geochemical phenomena (Peck 1961, 1975; LeGall and Postgate 1973). It should be noted that another process, assimilatory sulphate reduction, is also common to most plants and bacteria and involves the reduction of just enough SO_4^{2-} to HS^- to meet cellular requirements for sulphur containing amino acid biosynthesis (Peck 1961, 1975).

There are two main groups of sulphate reducing bacteria. Group one consists of Desulfovibrio, Desulfomonas, and Desulfotomuculum. These genera utilize lactate and occasionally pyruvate or ethanol as carbon sources. The second group consists of Desulfobulbus, Desulfobacter, Desulfococcus, Desulfosarcina, and Desulfonema. These genera, in contrast to those of group one, utilize the oxidation of the fatty acid acetate to derive their energy.

An example of the reaction pathways of Desulfovibrio in the oxidation of lactic acid and the dissimilatory reduction of sulphate is shown in Figure 5 (Laishley and Bryant 1987).

Also in the context of nonclassical sulphate reduction, some species of the genera Salmonella, Proteus, Camphylobacter, Succhuromyces, and Pseudomonas have been shown, in pure culture, to anaerobically reduce small amounts of SO_3^{2-} to HS^- (McCready et al. 1974; Brock et al. 1984). The role these organisms play in the cycling of inorganic sulphur in the ecosystem is not known at this time (Laishley and Bryant 1987).

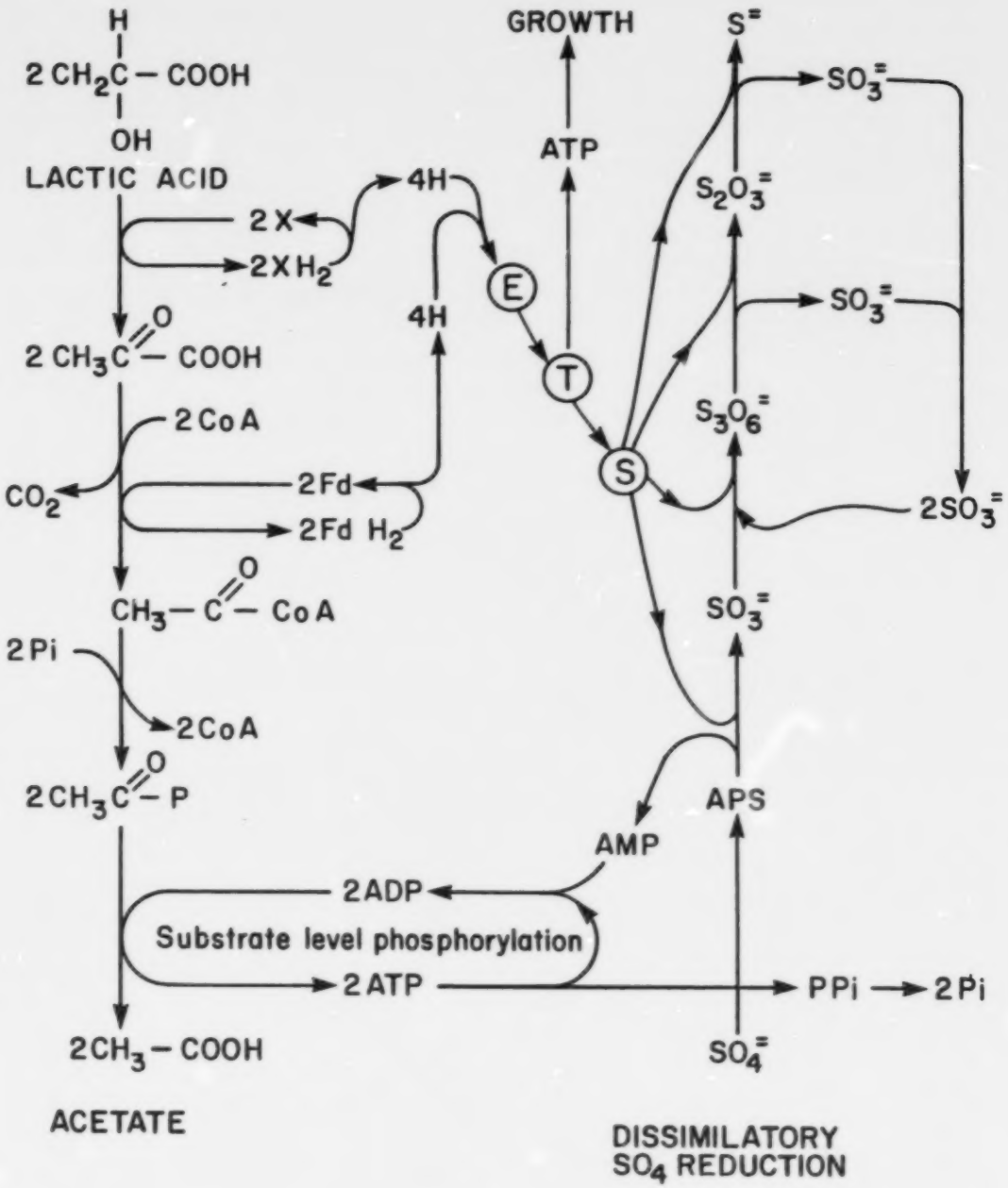

Figure 5. Oxidation of lactic acid and the dissimilatory reduction of sulphate by Desulfovibrio sp.

6.4 ECOLOGICAL AND ECONOMIC EFFECTS OF MICROBIAL INORGANIC SULPHUR OXIDATION AND REDUCTION

Laishley and Bryant (1987), in their review of sulphur microbiology, have discussed the ecological role of these microorganisms and their economic importance. Only the most important aspects will be discussed here.

As stated previously, Thiobacillus species oxidize elemental sulphur and in the process, produce sulphuric acid which can cause soil acidification. As long as the amount of sulphur available for oxidization is limited, this increase in soil acidity can benefit plant growth by providing not only more sulphate, but also more micronutrients because in the process of acidification, Ca, Mg, P, and K are also released (Gorham 1976; Wainwright 1978). Other advantages of sulphur oxidation are an increase in fertility in basic soils and protection from diseases such as potato blight (Starkey 1966). The addition of controlled amounts of elemental sulphur as a method of improving soil fertility in soils with pH 8 to 9 has been suggested and tried experimentally (Adamczyk-Winiarska et al. 1975; Bollen 1977; and Legge et al. 1986). The results of the tests showed a rapid reduction in soil pH as a result of the additions.

If large amounts of acid are added to a soil system the resultant lowering of the pH can adversely affect the soil microflora. A reduction of heterotrophic bacterial populations is one effect of such inputs (Adamczyk-Winiarska et al. 1975; Wood 1975; Bryant et al. 1979; and Wainwright 1979). Bryant et al. (1979) have also shown that the respiratory activity of microflora responsible for the degradation of glucose, starch, cellulose, casein, and urea was significantly reduced in soils exposed to simulated acidic rain of pH 3.0. Tamm (1976) reported that acidification inhibited the nitrification process in a forest soil while other workers have demonstrated that nitrogen fixation was inhibited under acidic conditions (Oden 1971; Dochinger and Seliga 1975). In addition, Tamm (1976) suggested that mycorrhizal fungi are very sensitive to acidic conditions. However, as noted earlier, most fungi are not acid sensitive.

6.4.1 Oxidation of Metal Sulphides in Soil

A number of environmental and agricultural problems occur as a result of chemolithotrophic oxidation of pyrite (FeS_2), a compound commonly present in coal and coal mining effluents. Pyrite is also found in soils where hydrogen sulphide from bacterial reduction reacts with ferrous iron to form ferrous sulphide. This in turn can react with either elemental sulphur or sulphides to form pyrite (Metson et al. 1977). Pyritic soils are potential sites for acidification. If sites containing pyritic soils change from anaerobic to aerobic conditions, acidic soils called "cat clay" will be formed (Metson et al. 1977). Under aerobic conditions pyrite is oxidized to sulphuric acid, jarosite [$KFe_3(SO_4)_2(OH)_6$], ferric oxides, and ferric sulphate (Bloomfield and Coulter 1973; Metson et al. 1977; and Kargi 1982). Pyrite may also be subject to oxidation by certain species of Thiobacillus. There are two basic mechanisms by which pyrite is oxidized; these are the direct and the indirect methods as shown in Figure 6. All of the reactions in Figure 6 utilize Thiobacillus ferroxidans to complete the oxidation.

DIRECT AND INDIRECT OXIDATION MECHANISMS FOR PYRITE OXIDATION

DIRECT

(1) $2\,FeS_2 + H_2O + 7.5\,O_2 \xrightarrow{\text{T. ferrooxidans}} Fe_2(SO_4)_3 + H_2SO_4$

Pyrite — Ferric sulfate

INDIRECT

(2) $2\,FeS_2 + H_2O + 7.5\,O_2 \xrightarrow{\text{T. ferrooxidans}} Fe_2(SO_4)_3 + H_2SO_4$

(3) $FeS_2 + Fe_2(SO_4)_3 \xrightarrow[\text{oxidation}]{\text{chemical}} 3\,FeSO_4 + 2\,S^0$

(4) $2\,S^0 + 3\,O_2 + 2\,H_2O \xrightarrow{\text{T. ferrooxidans}} 2\,H_2SO_4$

(5) $4\,FeSO_4 + 2\,H_2SO_4 + O_2 \xrightarrow{\text{T. ferrooxidans}} 2\,Fe_2(SO_4)_3 + 2\,H_2O$

Figure 6. Direct and indirect oxidation mechanisms for pyrite oxidation.

Other acidophilic thiobacilli may also participate in the oxidation of the elemental sulphur produced in reaction [3] in Figure 6 and thereby catalize the rapid formation of sulphuric acid. One of the more serious economic problems associated with sulphur microbiology results from this process and consists of the corrosion of metal, and weathering of stone and concrete (Parker 1947; Bryant et al. 1985).

Bacterial oxidation can also be beneficial. Pyrite oxidation has been used to extract sulphur from coal prior to combustion, thus lowering the emissions of sulphur oxides and the potential for acidic rain (Kargi 1982).

Thiobacillus ferroxidans is also used to leach copper from low grade ores. The process is similar to metal mobilization in soils. The bacteria grow by oxidizing ferrous iron to ferric iron. In the process they create a strongly oxidizing acid solution which in turn solubilizes and mobilizes other metals. Copper can then be reclaimed where other mining techniques would likely prove uneconomical (Brierley 1978).

6.4.2 Phototrophic Sulphur Bacteria

The photosynthetic sulphur bacteria provide the sulphur reducing bacteria with a substrate for growth without the consumption of molecular oxygen (Pfennig 1975; Postgate 1982). They also provide a food source for protozoa in lakes, thereby contributing to the secondary productivity of lakes (Sorokin 1970; Pfennig 1975).

In polluted waters the photosynthetic sulphur bacteria produce an excess of hydrogen sulphide causing in turn phototrophic blooms which, because of their colourful nature, have been suggested as indicators of water pollution (Postgate 1982).

6.5 FACTORS AFFECTING THE MICROBIAL OXIDATION OF SULPHUR

There are three main factors which influence the oxidation of elemental sulphur: the sulphur itself; the sulphur oxidizing microorganisms; and the nature of the soil environment where sulphur oxidation is occurring (Weir 1975).

6.5.1 Sulphur

Sulphur is a very complex and non-homogenous element. In studies conducted on "manufactured" sulphur, Laishley et al. (1984) produced three classes of sulphur by: (1) purifying production grade sulphur (B and F); (2) rapid cooling or quenching of molten B and F sulphur to form MMS (Mixed Molecular Sulphur); and (3) extraction of polymeric sulphur from sulphur using CS_2.

Laishley et al. (1984) showed that the B and F sulphur and the polymeric sulphur were oxidized by Thiobacillus albertis at similar rates while the MMS was oxidized at a much slower rate. It was clearly shown that the rate curves for these sulphur species began to diverge only after some 5% of the total sulphur was consumed (3 days). However, the MMS contained orthorhombic crystalline sulphur and polymeric sulphur well in excess of this percentage, indicating that the effect of the different molecular species in MMS was not simply related to the amount present. It has been suggested that the tightness with which the sulphur lattice is packaged could reduce the numbers of sterically favourable binding sites of T. albertis resulting in lower oxidation rates under certain conditions.

Laishley et al. (1983) have also shown that particle size determines the total amount of S that can be converted to sulphuric acid. Specifically, they found in their studies that T. albertis was capable of metabolizing 70% of a powdered sulphur with a particle size range of 150 μm to 250 μm, while only 3% of an equivalent weight of sulphur prill with a particle size range of 1.68 to 2.00 mm was metabolized. This type of information is critical from both a storage and shipping point of view for industries such as the sour gas processors. This indicates that large sized particles of sulphur will produce less acid and will also be more efficient for shipping because more product will reach its destination without being metabolized. Laishley et al. (1983) established the relationship that the microbial oxidation rate of sulphur was a function of the surface area per weight of sulphur.

Sulphur oxidizing microorganisms such as Thiobacillus have been shown to develop what are suspected to be acidic mucopolysaccharide polymer containing threadlike structures termed a "glycocalyx" which are utilized in substrate attachment (Takakawa et al. 1979; Costerton and Irvin 1981; Ladd 1982; and Bryant et al. 1983,1984). Bryant et al. (1983) believe that bacterial cells attached to the sulphur substrate by their glycocalyx produce microcolonies and eventually biofilms within the first few days of oxidation. This hypothesis was supported by Laishley et al. (1983) who observed with electromicroscopy cell surface processes and growth on prill sulphur, In comparison to powdered sulphur (70% oxidized) only 3% of the prill sulphur was oxidized over comparable time period. Laishley et al. (1983) also found that sulphate production remained linear over the duration of their experiment indicating that no exponential bacterial growth occurred as one would expect if the total substrate was available for metabolism by the oxidizing bacteria.

Based on the aforementioned experiments, Laishley and Bryant (1987) have proposed recommendations reducing environmental impacts caused by elemental sulphur via microbial oxidation. They suggested that elemental sulphur be stored in the solid block form and that production of powdered sulphur be minimized. Solid sulphur blocks would present a limited surface area to weight ratio which in turn would limit oxidation potential. This would increase the likelihood of biofilm development and would effectively insulate the block from further degradation.

6.5.2 Soil Environment and Its Effects on Sulphur Microbiology

Microbial oxidation of sulphur is influenced by temperature. Oxidation can occur below 10°C, although the rate will be slow (Weir 1975). Maximum rates of microbial sulphur oxidation have been reported at 40°C (Li and Caldwell 1966). Bryant et al. (1985) have shown that Thiobacillus albertis, a newly characterized acidophilic sulphur oxidizer, is non-functional at 5° and 37°C, and its optimum functional temperature is 28°C. At 37°C the bacterial activity is stopped and the cells are killed, whereas at 5°C the cells are not killed. These findings are significant when one considers the amounts of elemental sulphur stored in temperate climates where winter temperatures often reach the lower range but seldom exceed the upper range of tolerance. The experiments conducted by Bryant et al. (1985) showed that bacteria that were non-functional at 5°C could be revived by raising the temperature.

Soil type also influences the rate at which elemental sulphur can be oxidized. Laishley and Bryant (1987) cite the results of soil tests in Alberta that used elemental sulphur, sulphur concrete, and Portland cement in various locations throughout the province. After several years, thiobacilli were detected around the different sulphur substrates even though they were basically undetectable in some cases at the start of the experiment. A typical succession pattern was observed whereby the less acidophilic thiobacilli created an acid environment for the more acidophilic types that followed. Depending on the buffering capacity of the soil surrounding the test cylinders, the time required to detect pH changes ranged from 5 years at the most sensitive site, a forest soil, to no change on highly buffered alpine soil even after eight years of testing.

Sulphur oxidizing microorganisms are strongly affected by moisture conditions. Often in soils, moisture status is closely linked with the oxygen status. It is known that the thiobacilli will not grow in water-logged soils. Moser and Olson (1953) showed, however, that moisture levels near field capacity generated maximum microbial oxidation. Similarly, Laishley and Bryant (1985) observed that at moisture contents of <2% in a sandy loam site, the sulphur oxidizing activity of thiobacilli was low. Although the site contained sulphur substrates, the occurrence of these organisms was only sporadic over the eight years of study.

6.6 EFFECTS OF ACIDIC DEPOSITION ON SOIL MICROORGANISMS AND MICROBIALLY MEDIATED PROCESSES: LITERATURE CITED

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7. EFFECTS OF ACIDIC DEPOSITION ON GEOLOGY AND HYDROGEOLOGY

7.1 GROUNDWATER HYDROLOGY

The potential for geologic and hydrologic effects as a result of acidification have been reviewed by Campbell (1987). Many of the processes discussed by Campbell such as buffering capacity, cationic exchange, pH and the acidification process, metal mobilization, and toxicity have been previously discussed in this overview and, therefore, only the highlights of Campbell's report will be included here. A generalized view of the hydrologic cycle is shown in Figure 7.

The land-based portion of the hydrologic cycle is relatively well understood and although complex, is amenable to quantification. Groundwater hydrology is a measure of physical parameters essentially unaffected by chemical processes. Although groundwater hydrology plays a major role in influencing groundwater chemistry, groundwater hydrology itself is largely unaffected by geochemical processes. One can be reasonably certain that basin hydrology will be unaffected by geochemical processes that may be stimulated by acidic deposition. Therefore, one can conclude with confidence that the hydrology of a basin before acidic deposition will be the same as the hydrology of the basin after it occurs. However, the chemical constituents composing the basin waters may be totally changed.

Scientists who concentrate on the soils portion of the subsurface have tended to think of groundwater as a sink for soil leachate and that the problems of acidification were nullified once this system was reached. Recently, studies have shown that groundwater constitutes almost all of the base flow and a high percentage of peak flow from basin runoff. This is particularly important when one considers that in much of North America, winter flows in rivers are primarily of the base flow variety and, therefore, toxic metals have little opportunity to be diluted during this portion of the year. Therefore, in order to fully understand the chemistry of surface waters, it is essential that the groundwater chemistry also be considered. The ILWAS (Integrated Lake Water Acidification Study) mentioned in the sections on surface waters and soils (Sections 5 and 8 of this report), constitutes at present one of the most comprehensive examinations of receptor responses to acidic deposition. The results of ILWAS show that the routing of water through a watershed is the major determinant of lake water alkalinity and vulnerability to acidification as a result of deposition processes. These findings, therefore, dictate that any study of acidification and its effects must consider effects on groundwater, both surficial and deep, in order to produce viable results.

7.2 HYDROGEOLOGICAL NEUTRALIZATION PROCESSES

It has been recognized that acidic input into the land-based portion of the hydrologic cycle can be neutralized if sufficient quantities of buffering agents are present, and if the rate of neutralization can balance the rate of acidic input. With time, consumption of buffering agents by the various neutralization processes may lead to the exhaustion of the neutralizing ability of the soil-rock-water system. In attempting to quantify acidification or potential acidification, scientists have used a wide range of chemical descriptors including pH, alkalinity, cation exchange capacity,

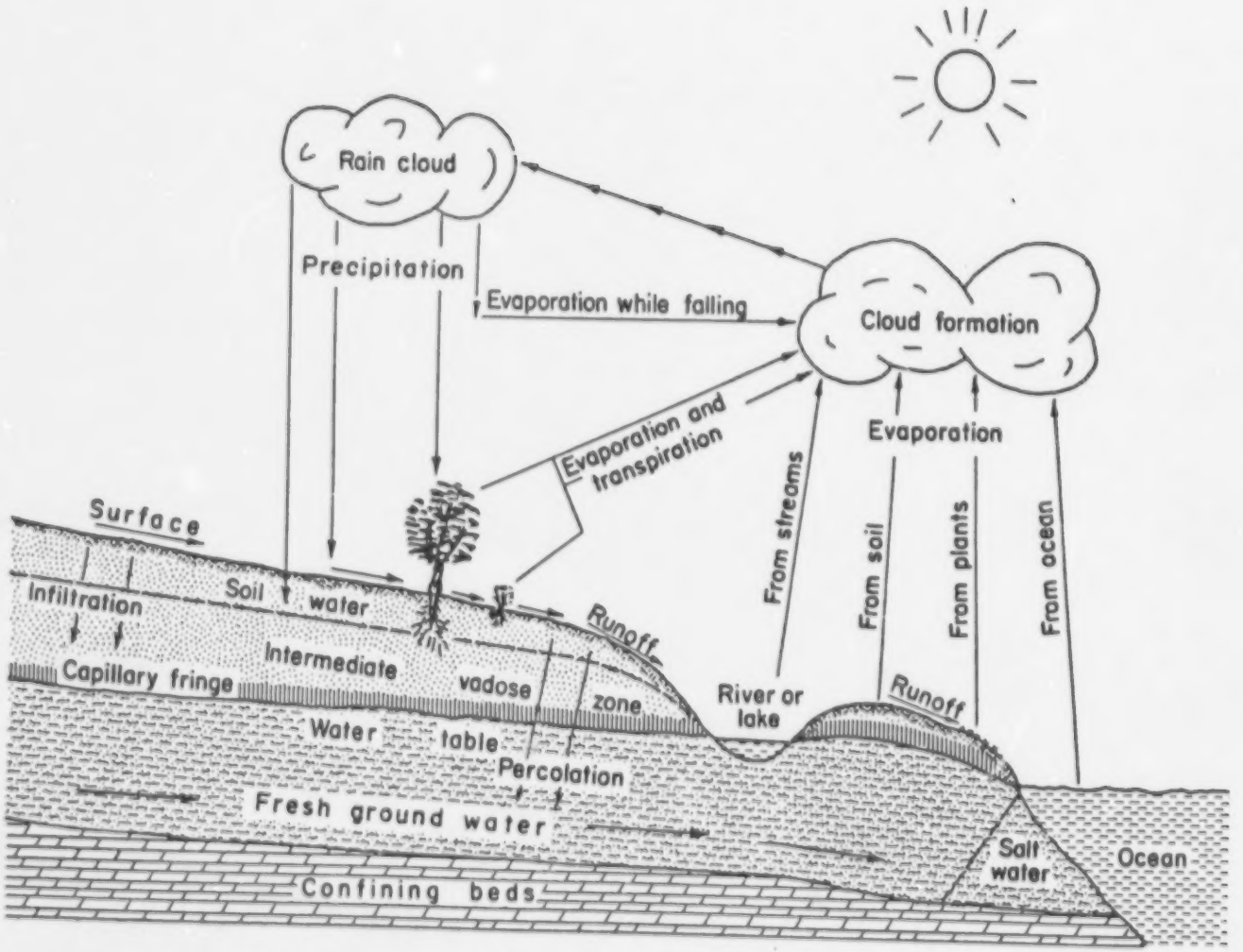

Figure 7. Schematic diagram of the hydrologic cycle. Source: Universal Oil Products Co. (1972)

buffering capacity, calcite saturation index, acid neutralization capacity, and lime potential. These descriptors are all described in detail in Sections 5 and 8 of this report.

As many as five types of neutralization processes may be active in the subsurface, (Last et al. 1980), but Bache (1984) has contended that the two major processes are cation exchange and acid hydrolysis reactions.

7.3 EVIDENCE OF GROUNDWATER ACIDIFICATION

Strong evidence of groundwater acidification has been observed in a number of Scandinavian studies. Evidence of groundwater acidification includes declining pH values and alkalinity as reflected in the bicarbonate values, coupled with an increase in calcium and sulphate. In the studies of Hultberg and Johansson (1981) and Jacks and Knutsson (1981), shallow aquifers with a low buffering capacity were most sensitive to acidification. In the La Holm region of Holland, up to 50% of the domestic water wells had a pH below 5.5 (Hultberg and Johansson 1981). In this study, several municipal water supplies in deeper aquifers also showed signs of acidification.

In Canada, analyses of water samples from wells in the Sudbury, Muskoka, and Haliburton areas of Ontario have not shown the same evidence of acidification as seen in Sweden. In each of the Canadian studies the systems lacked buffering capacity and have been exposed to long-term acidic deposition either from local sources and/or from long range transport. Only a small percentage of the water wells sampled in the Ontario studies showed depressed pH. It is conceded, however, that due to the heavy atmospheric loading of acidic materials in these areas and because of the low buffering capacity available for neutralization, with no change in the present loading, acidification of the groundwater will occur given sufficient time.

7.4 EFFECTS OF ACIDIC DEPOSITION ON MAJOR CATIONS AND ANIONS IN GROUNDWATER

The chemical constituents that are involved in the acid neutralization process are dependent upon the chemistry of the rock influenced water. The major cations and anions are: calcium, magnesium, sodium, potassium, carbonate/bicarbonate, sulphate, chloride, and nitrate. The role of each of these ionic species in the neutralization process is discussed in Sections 5 and 8 of this report.

Evidence is available to suggest that the following chemical changes may be observed upon acidification:

1. Increase in calcium concentrations;
2. Mobilization and increase in groundwater sulphate, if the adsorption capacity of the rock material is exceeded;
3. Mobilization and movement of chloride into the water table, resulting in increased groundwater concentrations;
4. Increase in nitrate with a net beneficial effect in nitrogen deficient soils. Once the nitrogen saturation of the subsurface waters is exceeded, nitrate may move to the water table. Once at the water table, no major attenuation mechanisms have been recognized;

5. Decrease in pH with an accompanying reduction in bicarbonate alkalinity; and
6. An increase in the concentration of dissolved aluminum, possibly accompanied by increased mobility of other dissolved metals.

7.5 EFFECTS OF ACIDIC DEPOSITION ON METALS IN GROUNDWATER

As noted in the sections on surface water (Section 8) and soils (Section 5) in this report, when pH levels decrease metals become increasingly mobile. This is particularly true in the subsurface between the pH values of 3.5 to 4.0. Metals of concern in subsurface waters are: aluminum, zinc, lead, copper, manganese, arsenic, chromium, cadmium, nickel, mercury, iron, and selenium. Because of the abundance of aluminum in rock materials and its highly toxic nature, this metal is of particular concern and is often used as an indication of acidification. Elevated aluminum levels have been detected in both surface and groundwaters in Sweden at locations where atmospheric loading has been heavy and acidification has been documented (Johansson and Hultberg 1977; Hultberg and Johansson 1978). Similar evidence has been found in studies conducted by Sharpe et al. (1984) in southern Pennsylvania. Studies conducted in eastern Canada have not as yet detected this trend in the subsurface waters except in a few samples. In most cases, metal concentrations were similar to background levels (Sibul and Vallery 1982; Sibul and Reynolds 1982). It should be noted, however, that the process of adsorption and precipitation may reduce the mobility of metals as they move from low to high pH environments. Therefore, it could be suggested that the subsurface waters have not as yet exhausted their buffering ability in those areas studied in eastern Canada and that the problem has not as yet reached the proportions of that found in Sweden.

Information currently available in the literature on the chemistry of heavy metals in natural waters and soils show that metal solubility in aqueous systems can be influenced by the following factors: organic materials, clay minerals, metal hydroxides, pH, and divalent ions.

7.6 PREDICTION OF ACIDIC DEPOSITION EFFECTS ON GROUNDWATER

7.6.1 Sensitivity Analysis

Early attempts to assess sensitivity of geographic areas to acidic deposition focussed on the ability of soil and rock materials to neutralize acidity (Shilts 1980, cited by Saskatchewan Research Council 1982; Glass et al. 1982). A major weakness of this approach is that it only addresses one portion of the ecological setting. It has subsequently been recognized that sensitivity of a geographic setting can only be assessed within the context of a multidisciplinary examination of the entire ecosystem. The present Acidic Deposition Research Program as represented by this overview is an attempt to take this latter approach to analysis.

7.6.2 Modelling

The development of hydrological and geochemical models is relatively well advanced. Presently, any number of computer models exist for simulating a wide variety of groundwater scenarios in both the saturated and unsaturated zones. In the past ten years, groundwater hydrology models have been coupled with mass transport models to

allow groundwater contamination problems to be simulated. Geochemical models which include PHREEQE, GEOCHEM, and GEOCHEM II allow the simulation of complex geochemical scenarios. The ILWAS has developed a model that has successfully simulated a variety of geochemical and hydrologic conditions of interest to researchers investigating the impacts of acidic deposition.

7.6.3 Human Impacts

Evidence presented to date indicates that there are identifiable issues concerning potential human health effects from acidification of groundwater. The three major areas of concern are:

1. The acidification of groundwater leading to alteration in the distribution of major cations and anions in domestic and municipal groundwater supplies with ensuing impact on the potability and aesthetics of the water supply.
2. The leaching of toxic metals from watersheds and from water storage and distribution systems.
3. The contamination of edible fish by toxic metals. Metals considered to be of concern include: lead, mercury, aluminum, copper, zinc, cadmium, chromium, iron, nickel, and selenium.

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8. EFFECTS OF ACIDIC DEPOSITION ON SURFACE WATER ACIDIFICATION

8.1 DETERMINATION OF ACIDITY IN SURFACE WATERS

Acidity is measured by two main methods, measurement of pH and measurement of alkalinity. Alkalinity is equivalent to the buffering capacity or increases in the ability to neutralize H^+. The major acid neutralizing species is HCO_3^- which combines with H^+ to form CO_2 and H_2O as follows:

$$HCO_3^- + H^+ \rightarrow CO_2\ (aq) + H_2O \qquad [19]$$

Alkalinity may be defined as the concentration of all hydrogen ion acceptors minus the free H^+ (Gherini et al. 1984). Thus:

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [\text{other } H^+ \text{ acceptors}] - [H^+]$$
$$= \text{ANC or Acid Neutralizing Capacity} \qquad [20]$$

In low alkalinity waters, the concentration of the other H^+ ion acceptors can become large relative to the total concentration of bicarbonate, carbonate, and hydroxide (Gherini et al. 1984). These other acceptors in such instances include the following species: organic compounds with carboxyl (-COOH) and phenolic hydroxyl groups (-OH), and the monomeric aluminum species and their complexes.

Following a series of iterations developed by Tetra Tech Inc. (1984), ANC in low alkalinity waters has been defined by the following equation:

$$ANC = \sum\text{cations} - \sum\text{anions} + 3Al_T \qquad [21]$$

where,

$$Al_T \text{ is total dissolved Al (mol } L^{-1}) \qquad [22]$$

The above equation maintains the charge balance between cations and anions in solution. In neutral waters, the concentration of dissolved aluminum is near zero which simplifies the equation as: cations minus anions. If the ANC value is negative, this is indicative of acidification. In acidic waters where dissolved aluminum is present, it must be included in the calculations or the ANC value will be incorrect (Tetra Tech Inc. 1984).

Recently, Herczeg et al. (1985) developed a new method for the monitoring of temporal trends in acidity which they claim avoids the problems of lack of sensitivity common with current technology. Their method is based on calculations of the equilibrium relationship between dissolved inorganic carbon and the partial pressure of CO_2. Herczeg et al. (1985) claim that this new method eliminates biases in pH as measured by electrode, and minimizes the effects of natural perturbations in acidity caused by biological activity and its effect on PCO_2.

8.2 SENSITIVE WATERS

Hendrey et al. (1980a) defined sensitive waters as those with alkalinities below 200 μeq L^{-1}, a level low enough to be neutralized by acidic deposition and runoff. Gibson et al. (1983) refined this classification to give the following ratings:

less than 50 μeq L^{-1}	- extremely sensitive
50 - 100 μeq L^{-1}	- very sensitive
100 - 200 μeq L^{-1}	- sensitive
greater than 200 μeq L^{-1}	- not sensitive

However, in other investigations, Canfield (1983) classified waters with alkalinities between 200 and 400 μeq L^{-1} as moderately sensitive. Various researchers have predicted the vulnerability of lakes and streams to acidification based upon these criteria (Gibson et al. 1983; Haines et al. 1983; Scruton 1983; Kling and Grant 1984; and National Wildlife Federation 1984).

The calcite saturation index, CSI, has been suggested as an improvement over alkalinity as a measure of aquatic system susceptibility to acidification (Kramer 1976; Galloway et al. 1978). The general form of this index is represented by the following formula:

$$CSI = -\log \frac{(Ca)\ (HCO_3)}{(H)K} \qquad [23]$$

where,

() are ion molar activities and

K is the equilibrium constant $CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$ [24]

Restructuring the formula gives the following form:

$$CSI = \log K - \log[Ca] - \log[HCO_3] - pH \qquad [25]$$

where log K = 2.582 - 0.242t, t being the temperature (°C).

Haines et al. (1983) have claimed that CSI is not superior to pH and alkalinity measures and is needlessly mathematically complex. Since the derivation of CSI is calculated from both pH and alkalinity, this seems to be a valid argument. Alkalinity is easily measured and even historical values can be readily recalculated if necessary, and it would appear that of the three types of sensitivity measurements available this should be the preferred method.

8.3 WATERSHED CHARACTERISTICS DETERMINING SURFACE WATER SUSCEPTIBILITY TO ACIDIFICATION

Lake acidification studies in the Adirondack Mountains, New York State, have clearly shown that all surface waters are not equally susceptible to acidification. A lake's vulnerability to atmospheric deposition depends upon its biogeochemistry and hydrology of its entire catchment area, including the type and condition of vegetation cover, bedrock characteristics, and the type and depth of soil (Goldstein et al. 1984a).

A summary of the watershed characteristics that influence surface water susceptibility to acidification and the precipitation pathways that must be considered when making an assessment of sensitivity are shown in Table 34 and Figure 8.

8.3.1 Major Determining Factors of Surface Water Acidity

8.3.1.1 Forest Canopy. The forest canopy interacts with and changes the chemistry of intercepted acidic deposition. This topic is dealt with at some length in Section 2 of this report (Forest Effects) and is only mentioned here to reiterate the need to consider this factor when assessing the impact or potential for impact of acidic deposition on surface waters.

8.3.1.2 Bedrock Geology. Bedrock geology has been most frequently used to assess potential susceptibility of surface waters to acidic inputs (Hendrey et al. 1980a; Kaplan et al. 1981). The chemical characteristics of the bedrock generally determine a region's susceptibility to acidification. Hendrey et al. (1980a) described four types of bedrock which distinguish susceptibility to acidification.

Type 1. Granite/syenite, granitic gneisses, quartz sandstones, or metamorphic equivalents. Low to no buffering capacity. High sensitivity.

Type 2. Sandstones, shales, conglomerates, high-grade metamorphic felsite to intermediate igneous rocks, calcsilicate gneisses (no free carbonates). Medium/low buffering capacity. Medium sensitivity.

Type 3. Slightly calcareous, low grade, intermediate to mafic volcanic, ultra mafic and glassy volcanic rocks. Medium/high buffering capacity. Low sensitivity.

Type 4. Highly fossiliferous sediments or metamorphic equivalents. Limestones or dolostones. High buffering capacity. Very low sensitivity.

Areas underlaid by limestone or other bedrocks high in calcite or other carbonaceous materials have extremely high buffering capacities capable of neutralizing extensive loadings of acids. Conversely, areas underlaid by granitic or related igneous rocks or their non-calcareous materials have an extremely limited buffering ability. Norton (1980, cited in Marcus et al. 1983) states that even small amounts of calcareous material in a watershed can exert enough buffering to change susceptibility from high to moderate in some watersheds.

8.3.1.3 Soil Type and Depth. Except when it falls directly on to surface waters or on to exposed bedrock, most precipitation percolates through or over soils prior to entry into the receptor waters. During the course of this passage, the chemistry of the waters can be changed substantially and this is the topic of the following section of this report (Section 5: Soils). Direct precipitation, surface runoff, and lateral flows from soil strata have their characteristic ranges of pH ranges and chemical species, and these are shown in a general way in Figures 9 and 10.

Table 34. Watershed characteristics that influence surface water susceptibility to acidification.

Category	Increased Susceptibility	Decreased Susceptibility
Bedrock geology	Resistant to weathering (metamorphic, igneous)	Easily weathered (sedimentary, calcite-containing)
Soils		
Buffering capacity	Low	High
Depth	Shallow	Deep
SO_4 adsorption capacity	Low	High
Topography	Steep-sloped	Shallow-sloped
Ratio of watershed to surface water area	Low	High
Lake flushing rate	High	Low
Watershed vegetation and land use		
Dominant vegetation	Coniferous	Deciduous
Forest management	Reforestation	Clearcutting
Water quality		
Alkalinity	Low (<200 $\mu eq/L^{-1}$)	High (>200 $\mu eq/L^{-1}$)
Trophic status	Highly oligotrophic	Less oligotrophic, mesotrophic, eutrophic
Cultural eutrophication	Forestry	Agriculture, municipal
Humic substances	Absent	Present
Sphagnum moss	Present	Absent
Sulfate reduction potential	Low	High
Climate/meteorology		
Precipitation	High	Low
Snow accumulation	High	Low
Growing season	Short	Long
Alkaline dusts	Low	High

Source: Marcus et al. (1983)

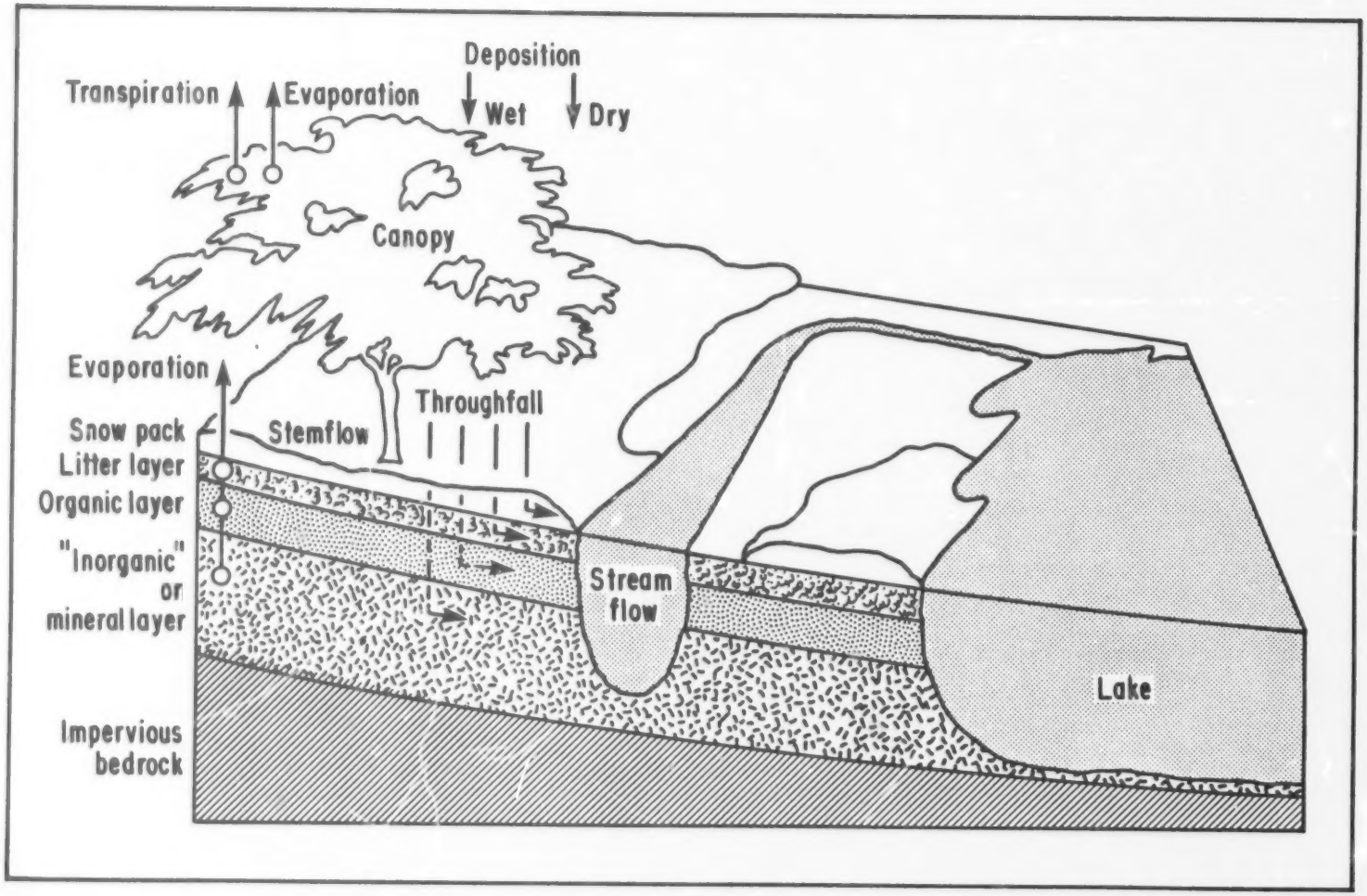

Figure 8. Precipitation pathways to a lake (after the ILWAS Study, Tetra Tech Inc. 1984).

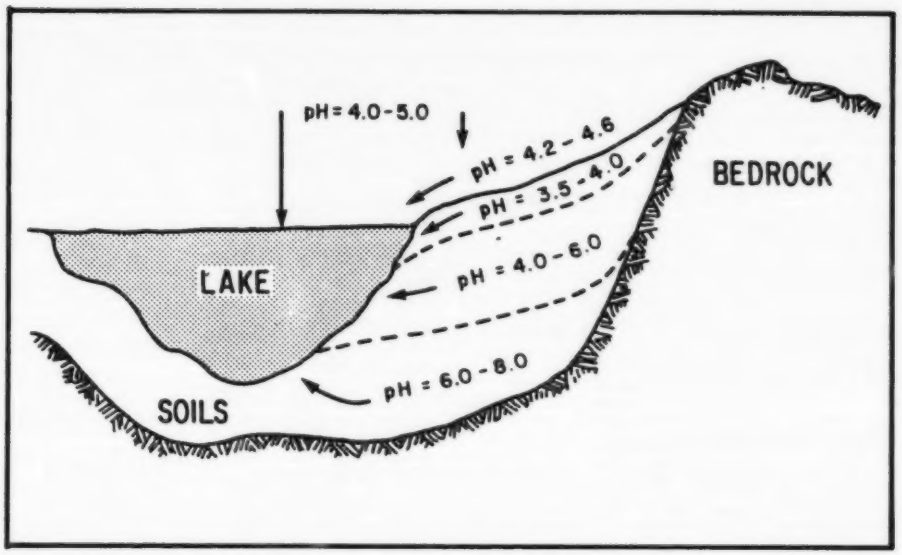

Figure 9. Lateral flow of water from different soil layers in determining lake water pH (after Chen et al. 1984).

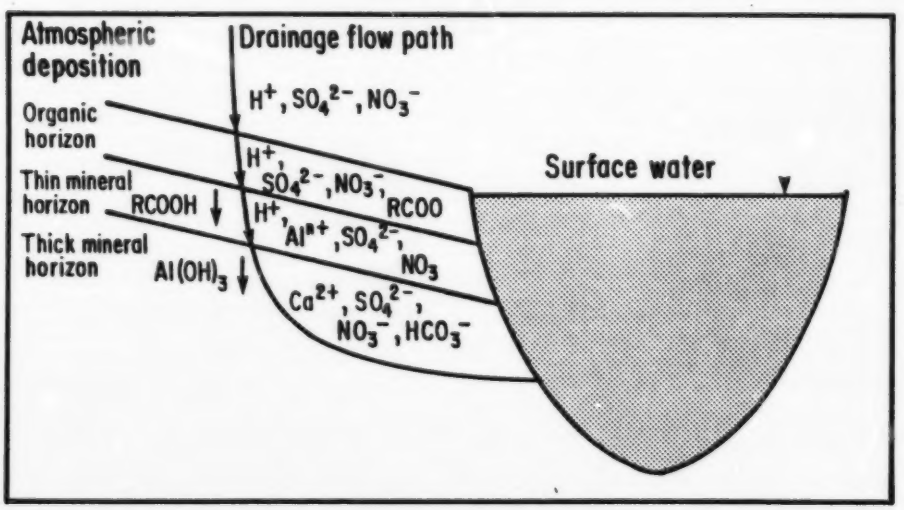

Figure 10. Chemical species associated with water flow paths to a lake (after Driscoll and Newton 1985).

8.3.1.4 Topography and Watershed-to-Lake Ratio. Both topography and watershed-to-lake ratio affect the susceptibility of surface waters to acidification (Panel on Lake Acidification 1984). During episodic events, these factors can influence or cause pH depressions of lakes and streams.

Watersheds with steep slopes or with little vegetation cover exhibit rapid runoff and are termed hydrologically flashy. Because of the rapidity of throughflow, it has been suggested that surface waters in such basins receive atmospheric precipitation largely unchanged in its chemical composition (Marcus et al. 1983). In systems with organic substrates through which the runoff passes either as overland flow or as percolation causing piston flow, the previous generalization may not be true. In either case, however, lakes or streams in such areas become more susceptible to acidification provided acidic deposition is occurring. A smaller watershed-to-lake ratio also increases susceptibility of lakes to acidification due to direct input of atmospheric deposition on its surface without the intervention of modifying agents. This process has been observed in Southern Ontario by Dillon et al. (1978).

Lakes in drainage areas with high watershed-to-lake area ratios tend to be less susceptible to acidification. This is primarily due to the basin's attenuation capacity and the longer time of contact with vegetation, soils, etc., all of which can ameliorate the effects of incoming acidic precipitation.

8.3.1.5 Watershed Vegetation and Land Use. Rosenqvist (1978b) and Krug and Frink (1983a,b) have claimed that terrestrial vegetation in watersheds markedly influences surface water pH. The effects of vegetation on both dry and wet acidic deposition is the topic of Sections 2 and 3 (Forests and Agriculture) of this report and should be consulted by the reader for the types of mechanisms and processes that incoming acidic deposition is subjected to, upon interception by vegetation and how this can have significant changes upon its ultimate chemical composition as it enters receptor waters.

8.3.1.6 Surface Water Quality. Alkalinity is the most important factor that determines the susceptibility of a water body to acidification. Waters with alkalinities lower than 200 $\mu eq\ L^{-1}$ have high susceptibility to acidification while alkalinities greater than 200 $\mu eq\ L^{-1}$ provide their basins with low susceptibility to acidification because of their high buffering capacity (Hendrey et al. 1980a). As discussed earlier, bedrock geology, soil, changing land use practices, and vegetation types generally influence surface water alkalinities. Runoff from agricultural lands which is high in nutrients and often lime, or from clearcut forest stands, appears to increase surface water alkalinity and pH, thus decreasing susceptibility to acidification (Rosenqvist 1978b; Braekke 1981). Decrease in alkalinity and pH can result from drainage originating from reforested lands or from agricultural areas subjected to ammonium and sulphate-containing fertilizers (Rosenqvist 1978b; Braekke 1981; and Hunt and Boyd 1981). In the first instance, the causes for decrease in the pH are related to organic acid formation by conifers and in the second, a result of microbial sulphur oxidation to sulphuric acid. These topics are dealt with further in Sections 2 and 6 of this report.

8.3.1.7 Climate and Meteorological Conditions. High precipitation areas are generally more susceptible to acidification because of the high leaching rate and consequently low cation exchange capacity usually found in such regions. This allows acidic input to pass through the system into receptor waters fairly quickly. Episodic events also contribute to acidification, in particular, snowmelt is considered important. Winter accumulations of acidic deposition and naturally produced acids are released to surface waters in fairly short pulses during snowmelt and have been observed to produce acid shock as a result, particularly in fish. Alkaline dust in the atmosphere can also influence the acid-base status of lakes. Increases in the quantities of alkaline dust tend to reduce the acidity of atmospheric deposition, a frequent phenomenon throughout the western portion of North America (Marcus et al. 1983).

8.4 ACIDIC WATERS AND THEIR REACTION PRODUCTS

Acidification of waters may be defined as a loss or decrease in acid neutralizing ability as measured by alkalinity. The major source of alkalinity in water is the bicarbonate ion which is produced by carbonic acid weathering of the surrounding bedrock and soil. The most common reactions resulting in weathering of limestone, dolomite, and silicates are:

1. $H_2O + CO_2 \rightarrow H_2CO_3$ [26]

2. $CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$ or $Ca^{2+} + 2HCO_3^-$ [27]

3. $CaMg(CO_3)_2 + 2H_2CO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$ [28]

4. $CaAl_2Si_2O_8 + 3H_2O + 2CO_2 \rightarrow Ca^{2+} + 2HCO^{3-} + Al_2Si_2O_5(OH)_4^{4-}$ [29]

In recent years, alkaline lakes considered to be sensitive, however, have been reported as acidic due to atmospheric deposition particularly of sulphuric and nitric acids.

Acidic substances in the atmosphere can reach surface waters through three pathways: (a) direct deposition from the atmosphere as dry and wetfall; (b) indirectly via runoff over or through the watershed; and (c) through internal generation within the watershed itself, for example, acidification of soils which in turn leads to the acidification of the water (Marcus et al. 1983; and Mason and Seip 1985). If, as a result of the loading of H^+, the overall alkalinity is depressed, the mobilization of potentially toxic heavy metals may also occur. For example, if pH is depressed to values between 4 and 5, ionic forms of aluminum, zinc, and lead, to name a few, may be released from the sediments. Above a pH of 6.5, these metals generally precipitate out of the water and are also absorbed by the sediments.

Acids deposited on the land result in competition between H^+ and CO_3^-. The net effect of this action is the leaching of bicarbonate, calcium, and magnesium ions causing the soils to lose buffering ability and eventually reducing the pH of the soil. As the atmospheric deposition continues and mineral, strong acid-weathering takes over from carbonic acid weathering, metals such as aluminum become mobilized. In this instance, the products reaching the aquatic environment are not H^+ ions but byproducts of reactions caused by soil acidification. Other types of alterations may also occur,

most notably in the cation exchange processes in the soil, whereby H^+ is exchanged with metal cations. It has been suggested that cation exchange occurs very rapidly if the H^+ is in solution, whereas the release of cations from other mineral sources is slow (Panel on Lake Acidification 1984). These types of reactions involving cations occur only in soils in which the cation exchange capacity is higher than 20 $\mu eq/100\ g^{-1}$. Below this value, H^+ may be exchanged more slowly or not at all, thereby accumulating in the soil. If the H^+ concentration continues to increase and the soil pH drops below 6.0, toxic metals such as aluminum become more soluble and are mobilized. Aluminum, for example, may be mobilized as free aluminum, or as a complex with fluoride, hydroxide, sulphate, or organic ligands (Driscoll 1980). The solubility of aluminum and other metals is highly pH dependent and its inorganic form determines whether its concentration increases with either increasing acidity or alkalinity (Driscoll 1980).

Hydrogen ions may also be generated internally by humic substances in the soil. This internally produced H^+ can also mobilize heavy metals by means similar to those outlined above for weathering (Krug and Frink 1983b).

The contribution of H^+ to the aquatic environment is, therefore, the sum of internally produced ions plus those remaining after weathering and ion exchange processes. This portion of acidity is combined with leached metal ions and mobile anions such as sulphate, nitrate, and organic anions. Since, in most cases, only a small fraction of acidic deposition falls directly on a lake relative to the land surface, surface water acidification depends primarily (but not solely) on the flow path that precipitation follows in a watershed prior to reaching the water body.

Cation and anion balance is the rule when ions are transported from soil to the aquatic environment so that electrochemical neutrality is maintained. Anions, such as sulphate and nitrate, are provided by acidic deposition. Although sulphate ions (SO_4^{2-}) are quite mobile, their mobility in a soil depends on its sulphate adsorption capacity (SAC). Most sulphate will be retained if the SAC is undersaturated (Galloway et al. 1984). Drablos and Tollan (1980) have reported that little retention of sulphate occurs in many North American or Scandinavian watersheds. Nitrate ions (NO_3^-) are also quite mobile, but their mobility depends on biogeochemical processes such as uptake by vegetation (Overrein et al. 1980) and on the velocity of water movement. During storm events when discharge and velocity of water increases, nitrate ions become highly mobile. However, in most instances, sulphate tends to be the major anion balancing cations with contributions being made by organic acid anions from internal generation or via acidic deposition. By means of oxidation processes, naturally occurring minerals such as pyrite, and NH_4^+, can also contribute sulphate and nitrate ions.

In summary, in areas receiving neither acidic deposition nor marine salts in precipitation, calcium and magnesium should be derived solely from weathering and leaching processes associated with carbonic acid and organic acids. The addition of calcium and magnesium ions in such cases should be electrochemically equivalent to alkalinity. In areas receiving acidic deposition, additional calcium and magnesium may be leached and an excess of hydrogen ions may cause reductions in alkalinity. Lakes in such watersheds exhibit calcium plus magnesium equivalences greater than alkalinity, and the excess cations are balanced by non-marine sulphate and nitrate (Almer et al. 1974; and Dickson 1980).

8.5 PRECIPITATION QUANTITY AND QUALITY AS FACTORS IN SURFACE WATER ACIDIFICATION

As stated previously, there are three general pathways for acidic substances to enter aquatic systems. Disagreement exists in the literature due to the lack of quantitative data documenting the contribution from each source. Gorham and McFee (1980) recognized this deficiency and suggested mass balance studies to determine the origins of acids, metals, and organic molecules entering aquatic ecosystems. Several studies are attempting to do this either by direct measurement or by predictive estimation using models (Dillon et al. 1982; Wright 1983; and Gherini et al. 1984). Of these studies, Gherini et al. (1984) using the model developed in the Integrated Lake-Watershed Acidification Study (ILWAS) actually attempted to quantify contributions for each routing in a mass balance.

In ILWAS a model was developed for two lakes in the Adirondack Mountains. Simulation of the model showed that routing of waters through soils (shallow versus deep flow) largely determined the extent of lake acidification. Analysis of the basins of the two modelled lakes, combined with field data, indicated that the internal production of acidity was approximately two-thirds the amount of atmospheric loading.

Likens et al. (1977) observed that hydrogen ion concentrations in Hubbard Brook were directly correlated with discharge volumes (r^2=0.73). They further suggested that observed increases in H^+ could be partially explained by the amount of precipitation. Rosenqvist (1978b), working in southern Norway, reported that following a storm event the pH in a stream dropped from 5.6 to 4.4, resulting in a pH shift equivalent to 5 times the acidity of rainwater entering the system. He attributed the pH shift to cation exchange processes in the soil and increases in leaching rates of naturally occurring hydrogen ions due to overland runoff and shallow groundwater throughflow.

The observations of Likens et al. (1977) and Rosenqvist (1978b) suggest that changes in stream chemistry during and immediately following precipitation events are greatly influenced by soil chemistry rather than solely by the H^+ concentration in the incoming rainfall. For example, large amounts of H^+ and Al_3^+ occur in soluble form in the naturally acidic environment of a coniferous forest, and all that is required to flush these chemicals through the system is a storm event of sufficient magnitude. Large amounts of these materials will be washed through the O and A soil horizons, where they are mostly produced, particularly if the terrain is steep and the storm is intense enough.

According to Elzerman (1983), changes in the chemical composition of stream water during precipitation events are important for the following reasons:

1. Significant portions of total annual fluxes of dissolved and particulate materials can occur during and following precipitation events;
2. Some products of neutralization and other reactions of rainwater with watershed components will appear in stream waters; and
3. Episodes in chemical composition above threshold values may occur; for example, transient events in which aluminum reaches toxic concentrations.

Elzerman (1983) studied the effects of precipitation events on the chemical regime of a watershed in South Carolina. He observed that during the precipitation events, in comparison to pre-event levels, pH dropped slightly (0.6 units), as did the concentration of bicarbonate ion (198 to 147 μeq L^{-1}). The major cations, Mg^{2+}, Ca^{2+}, and Na^{+} were reduced in concentration as a result of dilution and this in turn accounted for the slight acidification of the stream. The concentrations of sulphate and aluminum, on the other hand, increased from 8.5 to 143 and 10 to 100 μeq L^{-1}, respectively.

The quality of incoming precipitation can also potentially affect surface water chemistry. Lunde et al. (1977) detected more than 450 organic compounds in precipitation over Norway. These compounds, all of which were suspected to be from anthropogenic sources, consisted of: alkanes, polycyclic aromatic hydrocarbons, phthlates, fatty esters, aldehydes, amines, pesticides, and polychlorinated biphenyls (Lunde et al. 1977; Strachan and Huneault 1979; and Alfheim et al. 1980). Haines (1981) suggested that they were likely involved in acidic precipitation. However, such compounds, unless present as organic acids, do not contribute to surface water acidification.

Within Canada, impacts of atmospheric deposition on watersheds are most apparent in association with point source emissions. The best documented cases are found in the area surrounding Sudbury, Ontario (in relation to smelter operations) and in Halifax County, Nova Scotia. Harvey (unpublished work in Beamish 1976) found that sulphate concentrations in over 100 lakes in the Sudbury area were indirectly related to the distance from sources. Nickel and copper concentrations in lakes of the La Cloche Mountains, southwest of Sudbury, were found to exhibit similar trends (Beamish 1976); ranges in nickel and copper concentrations were 5 to 15 and 2 to 4 μeq L^{-1}, respectively, in affected lakes and less than 3 and 2 μeq L^{-1}, respectively, in remote lakes.

Watt et al. (1979) compared concentrations of hydrogen and sulphate ions in 116 lakes from Halifax Country, Nova Scotia and found results similar to those reported by Beamish (1976), that concentrations decreased with increasing distance from emission sources. In comparison to studies conducted 21 years previously, Watt et al. (1979) also found that the lakes were significantly more acidic. The decrease was related to the geomorphology of the lake basins studied. They found that pH decreased by approximately 0.34 units in granitic basins and by 0.65 units when the basin was composed of metamorphic rock. The 1955 pH values of the lakes studied indicated that none were well buffered and had original mean pH values of 4.66 on granitic and 5.62 on metamorphic rock. Similar results were obtained for sulphate concentrations. In granitic basins, sulphate concentrations increased by about 27.91 μeq L^{-1}, whereas in metamorphic basins, the increase was 47.5 μeq L^{-1}.

In addition to the aforementioned ions, increased concentrations of heavy metals have also been identified in relation to the loadings of point source emissions. Metals most often affected are lead, zinc, manganese, iron, nickel, mercury, vanadium, aluminum, and cadmium (Gorham and McFee 1980). Haines (1981) observed that metal concentrations were higher under conditions of acidic rather than non-acidic precipitation. Metal concentrations close to emission sources were the highest, but elevated concentrations were also observed far from identifiable sources. This suggests either long-range transport or increasing scavenging from the atmosphere as a result of acidic precipitation, or due to dry deposition or a combination of all three. Tomlinson et al. (1980)

pointed out that increased acidity of precipitation strips mercury from the atmosphere, the mercury likely originating from natural sources.

Snowmelt also affects surface water quality and has been studied by numerous authors in the context of acidic deposition (Galloway et al. 1980; Hendrey et al. 1980b; Johannes and Altwicker 1980; Johannessen et al. 1980; Bjarnborg 1983; Cadle et al. 1984; and Schofield 1984). Snow pH may be as low as 3.3, but in general values range from 4.5 to 5.0 (Seip 1980). The rapid release of acids from snow during a thaw can cause a rapid drop in the pH of poorly buffered lakes and streams. This phenomenon is termed acid shock and can have severe and drastic effects on aquatic life (Schofield 1976a,b; Hultberg 1977). Studies have shown that sulphate is preferentially leached from snowpacks during the winter making nitrate the dominant ion during the melt (Johannessen et al. 1980). Nitrate is biologically active. However, it is difficult to ascertain its importance in stream and lake acidification. Aging snow has also been found to become progressively less acidic, perhaps as a result of cation exchange with organic debris entrapped in the pack (Hornbeck et al. 1977).

During the first stages of the spring flush, higher concentrations of ions have been detected in stream waters in comparison to the snow pack itself (Hendrey et al. 1980b; Johannes and Altwicker 1980; and Cadle et al. 1984). As the snow pack melts, significant proportions of the major acidifying species are released during the loss of the first 21-35% of the pack. It has been suggested that melt occurs in three stages which can explain the resulting effects on stream water chemistry (Johannessen et al. 1980). During the first stage, old basin waters are pressed out of the system by piston flow which releases weathered ions such as calcium, magnesium, and bicarbonate, causing their concentrations to rise. It is followed by dilution of the ions during the second stage by the rising meltwaters containing low concentrations of weathered ions but high concentrations of acidic ions. The third stage consists of the remaining snowmelt which is relatively dilute in ionic content, thus causing a further dilution effect.

Jeffries et al. (1979) showed that hydrogen ion discharges from Canadian watersheds varied proportionately with discharge volumes during the two-month snowmelt period. It was found that runoff acidity was not relatively high in the early periods of snowmelt as was expected. This suggests that sources in addition to the snow pack accumulation, such as soil leaching, contributed to the discharge hydrogen ion loadings. Seip (1980) also felt that increased hydrogen ion concentrations in snowmelt waters reflect not only snow accumulations but also the influences of accumulations over winter in the soil. Soil-meltwater contact is extremely important in determining the final chemistry of thaw waters. Factors identified by Seip (1980) as contributing to this are soil freezing, air temperature, thickness of snow cover, texture of soil, and type of vegetation. Vegetation is most important in organically rich areas or in areas such as coniferous forests where the litter layer is naturally acidic. Seip (1980) states that this type of situation results in the leaching of organic acids which can then contribute substantial quantities of hydrogen ion to the meltwater.

Schofield (1984) reported on the temporal acidification of three lakes in the Adirondack Mountains during snowmelt. He attributed the observed effect to base cation dilution and to increased strong acid associated anion levels, particularly nitrate.

These changes in surface water chemistry were related to an upward shift in flow paths from groundwater dominated base flow (mineral horizon) to shallow humus layer flow during increased snowmelt as the shallow layers became saturated.

The literature surveyed clearly indicates that episodic events and factors of precipitation quantity and quality affect surface water acidification. The literature is still not definitive on how actual acidification occurs or the processes by which surface waters are acidified.

8.6 POTENTIAL SOURCES OF ACIDIFICATION OF SURFACE WATERS

Considerable controversy exists in the literature regarding surface water acidification. Most of the discussion revolves around the cause and effect relationships of acidification with regard to origin of the problem and whether it is anthropogenic or natural. Research that supports the theory that acidification is mostly anthropogenically derived may be found in Beamish et al. (1975), Overrein et al. (1980), Rahel and Magnuson (1983), and Somers and Harvey (1984). The theory that land use practices and/or internal proton production in soils cause acidification is supported by Rosenqvist (1978a,b), and Krug and Frink (1983a,b). Following a review of both types of literature, we feel that both points of view are valid but that anthropogenically induced land-soil-water acidification likely accelerates natural acidification processes in some instances.

8.7 TRENDS IN SURFACE WATER ACIDIFICATION IN NORTH AMERICA

Numerous studies conducted throughout North America were reviewed by Telang (1987). Only a few of these will be discussed in this overview and the reader is referred to the main body of Telang's text for further information on the studies outlined in Table 35.

In examining the trends in surface water acidification one must keep in mind the following points when comparing data sets:

1. Limited data are available for poorly buffered systems (Marcus et al. 1983);
2. Prior to 1955, pH was measured using colourimetric methods; more recently, potentiometric methods have been used;
3. Alkalinity was rarely measured prior to 1955 (Haines 1981);
4. Temporal differences and the effects of biological processes on pH were often ignored in historical and predictive studies when comparing data sets. For example, photosynthetic rates which reduce surface water acidity, and respiration which causes an increase in pH were factors often ignored. Studies conducted in Vermont on a soft water lake by Allen (1972) illustrated the importance of such factors. He found that pH changed from 5.65 to 9.57 between 0800 and 1200 hours and then decreased to 6.35 by 1600 hours on the same day.
5. Changes in land use practices were often ignored when comparing data sets and changes in acidity.

Table 35. Surface water acidification studies reviewed by Telang (1987).

Ontario (Beamish 1974, 1976; Somers and Harvey 1984; Keller et al. 1980; Glass et al. 1981)
Quebec (Jones et al. 1980: LaChance et al. 1985)
Atlantic Provinces (Watt et al. 1979; Scruton 1983)
Saskatchewan (Liaw 1982)
New England States (Haines et al. 1983; Marcus et al. 1983; Davis et al. 1978; Hendry et al. 1980a; Norton et al. 1981; Likens et al. 1977).
The Adirondack Mountains (Schofield 1976a,b; Pfeiffer and Festa 1980; ILWAS (Tetra Tech 1983, 1984; Driscoll and Newton 1985)
New Jersey (Johnson 1979a,b; Morgan 1984)
Virginia (Shaffer and Galloway 1982)
South Carolina (Elzerman 1983)
Florida (Brezonik et al. 1980; Canfield 1983; Flora and Rosendahl 1982)
California Sierra Nevada (Tonnessen and Harte 1982; Melack et al. 1982)
Upper Great Lake States (Eilers et al. 1983; Rahel and Magnuson 1983; Glass 1984)
Colorado Rocky Mountains (Lewis 1982; Turk and Adams 1983; Gibson et al. 1983; Harte et al. 1985; Kling and Grant 1984)

6. Most studies, except ILWAS (Tetra Tech Inc. 1983-84) have not included investigations of the major flowpaths that incoming precipitation follows within a basin prior to reaching a lake, or the major processes that take place along these paths that can and do alter the chemical characteristics of the throughflow waters.
7. The parameters of colour and dissolved organic carbon were often not included in studies of the trends in acidification of lakes and streams.

The parameters most commonly used to assess lake acidification have been acidity, alkalinity, concentration changes in base cations,and changes in aluminum concentrations. Some investigators report a trend in surface water acidification by comparing historical data and recent data on pH and loss of alkalinity, while others report lakes that may be susceptible to acidification based on bedrock characteristics and the present day lake or stream chemistry.

Surface water acidification studies in North America can be categorized into three groups. The first group consists of lakes for which the cause of acidification has been attributed to long range atmospheric transport and inputs of acidic substances. Studies conducted in the Atlantic Provinces, New England States, and New York State fall into this category. Within the second grouping of lakes, acidification has been attributed to the internal generation and contribution of hydrogen ions. Studies in the New Jersey Pine Barrens fall into this category. The third grouping consists of lakes for which acidification has not been established but predicted based on water chemistry and basin characteristics indicative of susceptibility. Lakes in the California Sierra Nevada and the Colorado Rocky Mountains fall into this category.

Keller et al.(1980) studied 200 lakes within a 200 km radius of the Sudbury smelter area and found that 30% of the lakes had a pH less than 5.5, while 40% had calcite saturation indices between 3 and 5, which are indicative of high sensitivity to acidification. The cause of acidification was attributed to smelter operations. Glass et al. (1981) suggested that about 6% of 1527 lakes surveyed in Ontario may be classified as acidic. Alkalinities in these acidified lakes were near or less than 0 $\mu eq\ L^{-1}$. Of the 103 acidified lakes, 83 are subjected to local loadings from smelter operations in the Sudbury and Manitoulin areas of the province. In the La Cloche Mountains, near Sudbury, Beamish (1974, 1976) found evidence of fish population losses which he attributed to acidification and heavy metal toxicity. He found that although concentrations of base cations did not show a significant difference between acidified and non-acidified lakes, calcium concentrations were twice as high in the first category of lakes. Acidified lakes also showed an overabundance of sulphate which represented 90% of the anion content of these lakes compared to values around 40% in non-acidified water bodies. These studies clearly indicated that lake acidification was caused primarily by local point source loadings from the smelter operations at Sudbury and the surrounding area.

Recently, Driscoll and Newton (1985) sampled twenty lakes and their watersheds in the Adirondacks in an effort to evaluate mechanisms that control the sensitivity of lakes to acidification. Two of the lakes were of the seepage variety with no inflow or outflow, and the other 18 were drainage lakes. The two seepage lakes and three of the

drainage lakes were then selected to illustrate the range of chemical composition found. The two seepage lakes received most of their water directly from precipitation and therefore were considered highly sensitive to acidic deposition. The pH values of the lakes were 4.7 for Barnes Lake and 4.3 for Echo Lake. Because these lakes received no runoff waters and were isolated from the groundwater system their concentrations of base cations and dissolved silica were very low. Despite their low pH values, both lakes also had low concentrations of aluminum. Differences in the physical and chemical characteristics of the lake basins were reflected in their chemistry. Barnes Lake, which is a perched clear water lake, received most of its acidity from atmospheric deposition and resulting in high sulphate concentrations. Echo Lake, however, while also receiving some acidic deposition, received the majority of its acidity from peat deposits, up to 28 metres thick, that surrounded the lake and released organic acids into its waters.

Of the three drainage lakes examined by Driscoll and Newton (1985), Merriam Lake was acidic (pH 4.5) as a result of a lack of base cations in its catchment area; West Pond was a bog lake (pH 5.2) whose acidity was mainly attributable to organic acid drainage plus acidic inputs via the atmosphere; and Cascade Lake (pH 6.5) was relatively insensitive to acidic deposition because of the balance maintained between atmospheric sulphate additions and high concentrations of base cations in its waters.

As a result of these studies, Driscoll and Newton (1985) suggested that sensitivity of lakes to acidification varies from lake to lake and that it depends on hydrology, mineralogy, and vegetative cover in the study area. They suggested that in the Adirondack lakes, organic acids were the main cause of brown water lake acidity, and that sulphuric acid, and to a lesser degree nitric acid deposition were the main causes of clear water acidity.

The longest continuous data base on stream water and precipitation chemistry in North America relates to the Hubbard Brook Experimental Forest in New Hampshire. This data base extends from 1964 to 1974 and has been reported by Likens et al. (1977). During the 10-year period, Hubbard Brook received acidic deposition with an average precipitation pH of 4.12. In addition, the area is classified as highly sensitive to acidification due to its bedrock geology and soil characteristics which indicate extremely low buffering ability. In spite of these factors, Likens et al. (1977) reported the maintenance of relatively constant stream water chemistry and no apparent trends in the stream pH, which remained near 5.0 over the study period.

8.8 EFFECTS OF ACIDIC DEPOSITION ON AQUATIC BIOTA

Acidification of freshwaters is a complex process involving not only increases in acidity but also increases in metal ion concentration, increased water clarity, accumulation of periphyton and detritus, changes in trophic interactions such as loss of fish as predators, and physiological changes in aquatic organisms. Magnuson (1983) has suggested that a study of the response of aquatic systems to acidic deposition must take into account all these types of changes because together they constitute the acidification process.

The impact of acidic deposition on aquatic biota was first observed in fish populations with the earliest record being from Norway where Atlantic salmon populations

began to decline in the 1920's (Jensen and Snekvik 1972). Since then, declining fish populations have been reported for many lakes and rivers throughout the world in areas receiving acidic deposition (Beamish and Harvey 1972; Drablos and Tollan 1980; and Schofield 1982). These fish extinctions were related to changes in water chemistry, particularly increases in acidity and heavy metal concentrations. Later, studies on the effects of acidification on aquatic organisms were broadened to include other trophic classes of organisms as well as fish.

Telang (1987) has reviewed this literature by first identifying those organisms commonly found in naturally occurring acidic waters, and then by documenting the experimental evidence for acidification effects caused by deposition. Organisms that occur in naturally acidic waters are shown in Table 36. This type of information provides a baseline from which to measure the effects of natural versus anthropogenically caused acidification. The results of numerous studies into the effects of acidic deposition on aquatic organisms may be found in Table 37 which indicates that the effects are varied and definitely not restricted to fish. In general, it appears on the basis of the experimental evidence (Table 37) that effects of surface water acidification on aquatic organisms becomes apparent as alkalinities decline to 65 $\mu eq\ L^{-1}$ and pH values decline to about 6.0. Baker (1983a,b) suggested that pH declines below this value would result in escalating biological changes such as loss of benthic species from the community, loss of fish species, and loss of community structural complexity. This last point is important because it would indicate that the resilience and ability of the biological community to withstand further change would also be lost such that future impacts may cause an exponential effect on overall system productivity. The effects of acidification also become apparent during episodic events when the pH of the water may drop from as high as 7.0 to 4.3 very quickly. Such an episodic event in many areas of North America results from snowmelt. Although acidic deposition can have detrimental effects on aquatic biota, it is only one of the many factors working jointly in the ecosystem to produce such effects. Others include natural acidic waters and acid forming processes, elevated levels of toxic metals, availability of nutrients, and changing land use practices.

8.9 MODELS OF FRESHWATER ACIDIFICATION

Three types of models have been developed to evaluate the acidification of freshwaters by acidic deposition. These include empirical models, static and dynamic mechanistic models, and conceptual models. Telang (1987) has reviewed a number of these modelling efforts from each category and found problems in all cases, with the possible exception of the ILWAS model. The ILWAS model is a dynamic model that is suggested to have potential for universal applicability. Only the ILWAS model will be discussed in the following section. The reader is referred to Telang (1987) for further details of the other models reviewed.

8.9.1 ILWAS Model

The Integrated Lake-Watershed Acidification Study (ILWAS) model was developed to provide a mathematical approach capable of predicting changes in surface water acidity given changes in the acidity of precipitation and dry deposition (Gherini et al. 1984;

Table 36. Lower pH limits for various groups of organisms in naturally acidic waters.

Group	Approximate Lower pH Limit	Examples of Organisms Occurring at Lower pH Limit	Reference
Bacteria	0.8	*Thiobacillus thiooxidans, Sulfolobus acidocaldarius*	Brock (1978)
	2-3	*Bacillus, Streptomyces*	Brock (1978)
Fungi	0	*Acontium velatum*	Brock (1978)
Eucaryotic algae	0	*Cyanidium caldarium*	Brock (1978)
	1-2	*Euglena mutabilis, Chlamydomonas acidophila, Chlorella*	Brock (1978)
Blue-green algae	4.0	*Mastigocladus, Synechococcus*	Brock (1978)
Vascular plants	2.5-3	*Eleocharis, Carex, Ericacean* plants	Brock (1978) Hargreaves et al. (1975)
		Phragmites	Ueno (1958)
Mosses	3.0	*Sphagnum*	Brock (1978)
Protozoa	2.0	Amoebae, Heliozoans	Brock (1978)
Rotifers	3.0	*Brachionus, Lecane, Bdelloid*	Hutchinson et al. (1978)
	3.5	*Colotheca, Ptygura*	Edmondson (1944)
Cladocera	3.0	*Simocephalus, Chydorus*	Ueno (1958)
Copepods	3.0	*Macrocyclops*	Ueno (1958)
	3.6	*Cyclops*	Hutchinson et al. (1978)
Insects	2.0	*Ephydra thermophila*	Brock (1978)
	3.0	*Chironomus riparius*	Hutchinson et al. (1978)
	5.8	Mayflies	Sutcliffe and Carrick (1973)
Amphipods	5.8	*Gammarus*	Sutcliffe and Carrick (1973)
Clams	4.5	*Pisidium*	Griffiths (1973)
	6.0	Most other species	Pennak (1978)
Snails	5.8	*Amnicola*	Pennak (1978)
	6.2	Most other species	Pennak (1978)

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Table 36 (Concluded).

Group	Approximate Lower pH Limit	Examples of Organisms Occurring at Lower pH Limit	Reference
Fish	3.5	*Tribolodon hakonensis*	Mashiko et al. (1973)
	4.0	*Umbra limi*	Rahel and Magnuson (1983)
	4.5	Sunfishes (Centrachidae)	Rahel and Magnuson (1983)

Source: Magnuson (1983).

Table 37. Effects of increasing acidity on aquatic ecosystems.

Taxon or Process	Type of Evidence: Field Observation	Field Experiment	Lab Experiment	Observed Effects
BENTHOS				
Molluscs (most species except fingernail clams, family Sphaeriidae)		-	-	The calcareous shell of these animals is soluble under acidic conditions, making this group highly sensitive to low pH. Few species present below pH 6.0 except for several species of fingernail clams which may persist down to pH 4.5-5.0.
Crayfish	Almer et al. (1978)	Mills (1982)	Malley (1980) *	In soft water lakes, calcium uptake and exoskeleton formation inhibited in pH range 5.0-5.8. Reproduction impaired at pH 5.4
Amphipods (Gammarus)	Okland (1980c) Sutcliffe & Carrick (1973)	-	Costa (1967) Borgstrom & Hendrey (1976)	Absent below pH 6.0. In the laboratory avoids pH 6.2 and lower.
Mayfly larvae (Ephemeroptera)		Hall et al. (1980)	Bell & Nebeker (1969) Bell (1971)	Most species decline or are absent in pH range 4.5 to 5.5.

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Table 37 (Continued).

Taxon or Process	Type of Evidence: Field Observation	Field Experiment	Lab Experiment	Observed Effects
Water striders (Gerridae), backswimmers (Notonectidae), waterboatmen (Corixidae), beetles (Dytiscidae, Gyrinidae), dragonflies (Odanata).	*	-	-	Tolerant of acidity. Increase in abundance in acidified lakes (below pH 5.0) after other invertebrate groups and fish have been eliminated.
Benthos community structure	*	Hall et al. (1980)	Bell & Nebeker (1969) Bell (1971)	With increasing acidity, species richness declines. Entire groups of aquatic organisms are absent or poorly represented below pH 5.0 (e.g., molluscs, amphipods, crayfish, mayflies). Other taxa become dominant, particularly after loss of fishes (e.g., predacious beetles and true bugs).
Benthic algae (periphyton)	*	Hall et al. (1980) Schindler (1980)	Hendrey (1976)	Algal mats overgrow rooted plants and cover bottom substrates in acidified lakes below pH 5.0

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Table 37 (Continued).

Taxon or Process	Type of Evidence: Field Observation	Field Experiment	Lab Experiment	Observed Effects
MACROPHYTES				
Eriocaulon sp. Lobelia sp.	Grahn (1977) Best & Peverly (1981) Miller et al. (1982)	-	Laake (1976)	Rosette plant communities may become overgrown by algal mats. Tissue aluminum concentrations increase as pH decreases. Photosynthesis of rosette species decreases by 75% as pH declines from 5.5 to 4.0.
Daphnia	*	-	Davis & Ozburn (1969) Parent & Cheetham (1980)	Most species are acid-sensitive and absent below pH 7.0 to 5.5.
Zooplankton community structure	*	-	-	The number of species declines as acidity increases. Taxa characteristic of acid conditions include certain genera of rotifers (Keratella, Kellicottia, Polyarthra); cladocerans (Bosmina); and copepods (Biaptonus).

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Table 37 (Continued).

Taxon or Process	Type of Evidence: Field Observation	Type of Evidence: Field Experiment	Type of Evidence: Lab Experiment	Observed Effects
Phytoplankton community structure	*	Yan & Stokes (1978)	-	The number of species declines as acidity increases. Dinoflagellates (Phylum Pyrrophyta) frequently dominate acidified lakes (pH 4.0-5.0). Dinoflagellates are a less palatable food source for zooplankton compared to the phytoplankton they frequently replace.
FISHES				
Fathead Minnow (*Pimephales promelas*)	Rahel & Magnuson (1983)	Mills (1982)	Mount (1973)	One of the most acid-sensitive fish species. Reproductive failure occurs near pH 6.0. Generally absent in waters below pH 6.5.
Darters (*Etheostoma exile*, *E. nigrum*, *Percina capnodes*) and Minnows (several *Notropis* spp. *Pimephales notatus*).	Harvey (1980)	-	Rahel & Magnuson (1983)	Very acid-sensitive. Generally absent below pH 6.0 in both naturally acidic and anthropogenically acidified waters.

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Table 37 (Continued).

Taxon or Process	Type of Evidence: Field Observation	Type of Evidence: Field Experiment	Type of Evidence: Lab Experiment	Observed Effects
Smallmouth Bass (*Micropterus dolomieui*)	Beamish (1976) Harvey (1980), Rahel & Magnuson (1983)	-	-	Reproduction ceases and populations become extinct below pH 5.2-5.5.
Lake Trout (*Salvelinus namayeusch*)	Beamish (1976) Beamish et al. (1976)	Mills (1982)	Beamish (1972) Trojnar (1977a)	Experiences reproductive failure near 5.0. Generally absent below pH 5.0 in both naturally acidic and anthropogenically acidified waters.
White Sucker (*Catostomus commersoni*)	Harvey (1980) Rahel & Magnuson (1983)	Mills (1982)	-	
Rainbow Trout (*Salmo gairdneri*)			*	Adversely affected by pH's below 5.0-5.5.
Atlantic Salmon (*Salmo salar*)	*	-		Adversely affected by pH's below 5.0.
Brown Trout (*Salmo trutta*)	*	*	*	Lower pH limit between 4.5 to 5.0.
Brook Trout (*Salvelinus fontinalis*)		Hall et al. (1980)		Lower pH limit between 4.2 to 5.0.

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Table 37 (Concluded).

Taxon or Process	Type of Evidence: Field Observation	Field Experiment	Lab Experiment	Observed Effects
Sunfishes (*Ambloplites rupestris*, *Micropterus salmoides*, *Lepomis* spp.)	Harvey (1980) Rahel & Magnuson (1983)	Smith (1957)	-	Lower pH limit near 4.5.
Yellow Perch (*Perca flavescens*)	Svardson (1976) Keller et al. (1980) Harvey (1980) Rahel & Magnuson (1983)	-	Rahel (1983)	Lower pH limit 4.2 to 4.5. May become very abundant after other species have become extinct.
DECOMPOSITION	Hendrey (1976) Leivestad et al. (1976)	Scheider et al. (1976), Gahnstrom et al. (1980) Hall et al. (1980)	Leivestad et al. (1976)	Bacterial decomposition is significantly reduced in the pH range 4.0 to 5.0. In many cases, fungi replace bacteria as the primary decomposers.

* numerous research
\- not studied

Source: Magnuson (1983)

Goldstein et al. 1984b). The model was developed specifically to predict changes in surface water hydrogen and aluminum ion concentrations because of their importance to fish. It was divided into two modules: hydrological and chemical. The model incorporated the major flow pathways followed by precipitation and the major biogeochemical processes that alter the chemical characteristics of water as it moves along these pathways. The model accounted for the routing of the precipitation through the forest canopy, soil horizons, and streams and lakes using mass-balance concepts and equations which related flow to hydraulic gradients. The physical and chemical processes which change the acid-base status of the water were simulated by rate and equilibrium expressions. Mass balance transfers between gas, liquid, and solid phases were included in the model. The aqueous constituents simulated were the major cations and anions, aluminum and its complexes, organic acid analogues, and dissolved inorganic carbon. Concentrations of free hydrogen ion or pH were derived from the solution alkalinity and the total concentrations of inorganic carbon, organic acids, and monomeric aluminum.

The model was used to predict changes in acidity of Woods Lake (pH 4.7 to 5.1) and Panther Lake (pH 5.3 to 7.8) given reductions in the total atmospheric sulphur loads. A reduction in the incoming sulphur load by 50% was found to have little effect on the pH of Panther Lake even after a 12 year simulation; in Woods Lake, however, the pH increased substantially.

The model showed that movement of water through shallow or deep soil largely determines the extent to which incident precipitation is neutralized as reported by Chen et al. (1984) and Schofield (1984). Analysis of the two lake basins using the simulation model and field data showed the watersheds to be net suppliers of base to the throughflowing waters, and that the watershed internally provided two-thirds of the amount of the atmospheric acidity naturally.

The ILWAS model can be criticized for treating the role of internally generated organic acids simplistically. However, it is important to note that Schofield (1984) observed that organic acids were not important in determining the pH of the lakes studied in the ILWAS program.

It is also important to note that while the two study lakes were morphometrically similar, the model correctly identified the effects of the differences in soil characteristics and the resultant effect that would have on long term pH changes. Woods Lake is surrounded by thin till which is less permeable than that of the deeper tills surrounding Panther Lake. Thus, a large fraction of the throughflow water draining into Woods Lake moves through organically rich, shallow soil horizons, whereas similar waters in the Panther Lake drainage basin are in contact with base rich tills for a longer period. Therefore, the lateral flow waters entering Woods Lake after moving through the shallow organic horizons result in low pH and low alkalinity values. Removal of the incoming acid loading to the lake, which Gherini et al. (1984) had estimated to account for up to 60% of the total basin acidity would therefore allow the pH in Woods Lake to rise; conversely, the pH of the already well buffered waters of the Panther Lake Basin would not.

8.10 EFFECTS OF ACIDIC DEPOSITION ON SURFACE WATER ACIDIFICATION: LITERATURE CITED

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PART II.

ACIDIC DEPOSITION IN THE ALBERTA CONTEXT

9. ACIDIC DEPOSITION IN THE ALBERTA CONTEXT

9.1 MAJOR BIOPHYSICAL COMPONENTS OF ALBERTA

The major biophysical components of Alberta have been reviewed by Jaques (1987). These include 1:1,000,000 mapping of macroclimatic regions, physiographic regions, physiographic subdivision, bedrock geology, and vegetation for the province with the exception of the National Parks areas. Each bedrock formation in Alberta has been rated according to its potential buffering capacity with respect to acid deposition at a scale of 1:1,000,000. Rocks with low to no buffering capacity occur where relatively pure siliceous rocks of sedimentary, igneous, and metamorphic origin are found, and these are mainly in the northeastern portion of the province and along the Rocky Mountains and their foothills. The map also indicates the distribution of unlimited, high to medium, and medium to low buffering capacity in bedrock formations.

The twelve macroclimatic regions of the province recognized by Strong and Leggat (1981) are also mapped and the dominant vegetative species complexes within each have been identified. Jaques (1987) recognized 134 vegetation community types throughout Alberta. The community type analysis provided by Jaques (1987) shows that major climatologically controlled subdivisions occur in the province. These are: Subalpine, Montane, Parkland, and Boreal Uplands areas. Jaques suggests that similar subdivisions occur in other regions of the province but to date these have not been documented.

The sensitivity of macroclimatic and/or vegetation community types to acidic deposition was not provided in the documentation because of a lack of sufficient data on which to base such predictions at this time (Jaques 1987).

9.2 ACIDIC DEPOSITION AND ALBERTA FORESTS

Research into the effects of acidic deposition on forest ecosystems in Alberta is extensive and has been documented briefly in Table 38. These programs indicate that as a result of acidic deposition, soil acidification with accompanying solubilization of aluminum and manganese is becoming evident in some areas (Baker et al. 1977; Nyborg et al. 1977; Addison and Puckett 1980; and Addison 1984). Lore (1984), however, found no evidence of change in soil pH downwind from a sour gas plant near Pincher Creek, Alberta. The soils on which this study was conducted were of the loam to clay-loam variety, not likely to be sensitive to acidification. Studies such as those of Legge et al. (1977), Legge (1982), and Addison et al. (1984) have shown convincingly that photosynthetic capacity of major tree species can be reduced close to emission sources. These studies also indicate that there have been measurable effects at the biochemical level such as chlorophyll destruction and altered energy allocation in trees in close proximity to emission sources (Malhotra 1977; Harvey and Legge 1979). The literature also indicates that, overall, forest growth may be reduced as a result of acidic deposition in Alberta near point sources (Legge et al. 1984, 1986; Amundson et al. 1986). Non-point source contributions as a result of farming practices also contribute to acidification. Sanderson (1984) pointed out that agricultural fertilizers contribute approximately 25 times more to soil acidity on a yearly basis than does atmospheric deposition. This implies that fertilizers contribute more to potential soil acidity in Alberta than do industrial sources. An indication of the seriousness of this problem

Table 38. Alberta research references on the effects of pollutants on forest ecosystems.

Species or Soil	Research	Location	Reference
Not stated	Sampled precipitation, throughfall, and stemflow and soil solution. Soil acidity and extractable Al increased nearer the source. Precipitation acidified.	Rocky Mountain House and Fort McMurray	Baker et al. (1976) Baker et al. (1977)
Pinus contorta forest	Effect of elemental S dust from natural gas plant stockpile. Sites <200 m had elevated soil S in the upper 20 cm. Lowered pH and Mg, K, and Mn in LFH horizon. Mosses eliminated and herb cover reduced.	Rocky Mountain House	Addison et al. (1984)
Forest	Dry deposition of S may be more important than wet deposition.	Central Alberta	Nyborg et al. (1977)
Lichens	Branches of black spruce covered with transplanted lichens showed reduced cover over 3 years up to 8.3 km along a steep SO_2 gradient.	Fort McMurray	Addison (1984)
Hypogymnia	High levels of Al (3000-5000 mg Al kg^{-1}) and Mn (200-300 mg Mn kg^{-1}) in area with high SO_2.	Fort McMurray	Addison & Puckett (1980)
Aspen, Willow, Green alder, Paper birch, Jack pine, White spruce, Black spruce, Labrador tea	Fumigation with 15.2 µmol m^{-3} (0.34 ppm) SO_2 reduced net photosynthesis in all species and produced visible symptoms in 2 to 20 days. Response was less rapid in the conifers. Conifers on tailings sand responded more rapidly than on the native soil.	Plants from Fort McMurray	Addison et al. (1984)
Lodgepole x Jack pine hybrids	Foliage ATP levels decreased as SO_2 increased.	Trees from Whitecourt	Harvey and Legge (1979)
Pinus contorta	SO_2 (aq) destroyed chlorophyll	Edmonton	Malhotra (1977)

continued...

Table 38 (Concluded).

Species or Soil	Research	Location	Reference
Lodgepole x Jack pine hybrids, White Spruce and Aspen	Photosynthesis rates of the trees were lower than expected and corresponded to high SO_4-S levels in the leaves.	Whitecourt	Legge et al. (1977) Amundson et al. (1986)
Boreal forest	A 4 year case study involving air monitoring, isotopic studies, woody plant water relations, pine tree physiology, plant mineral nutrition, and plant biochemistry. Modifications to the forest ecosystem were documented.	Whitecourt	Legge et al. (1981) Legge (1982) Krouse et al. (1984) Mayo et al. (1986) Amundson et al. (1986)
Lodgepole x Jack pine hybrids	Analysis of tree rings from ecological analogs downwind from a sour gas plant by PIXE demonstrated that rings have a historical record of differences in elemental composition, presumably due to S gases.	Whitecourt	Legge et al. (1984)
Forest	Studied forest composition along pollution gradients away from the SUNCOR oil sands plant. No differences were found.	Fort McMurray	Pielou (1982)
Loam to clay loam	Soil pH measured for 9 years at locations downwind from a sour gas plant. There were no changes in pH.	Foothills near Pincher Creek	Lore (1984)

was pointed out by Torn et al. (1987) who suggested that liming practices would need to become common if the present fertility of Alberta soils is to be maintained, primarily to offset the effects of acidification caused by fertilization. This conclusion was also substantiated by Turchenek et al. (1987) in their review of the potential for soil acidification in Alberta.

In summary, Mayo (1987) stated that the effects of acidification documented for Alberta, to date, require clarification to determine whether or not they are direct or indirect effects and that a better understanding of forest processes is required to make these clarifications.

9.3 ACIDIC DEPOSITION AND ALBERTA AGRICULTURE

Agricultural production contributed 10.2% of Alberta's gross domestic product in 1981, with grain crops such as wheat and barley accounting for over 75% of Alberta's farm cash receipts. Almost 30% of Alberta's land area is used for farming, with 12% being cultivated at a given time (Alberta Agriculture 1982). Ecologically, agriculture and grazing are dominant in four ecoregions of Alberta: Short Grass, Mixed Grass, Fescue Grass, and Aspen Parkland, which in total cover about 25% of the province (Strong and Leggat 1981). Thus, the effect of air pollutants on agriculture is of both ecological and economic concern.

The Clean Air Act of Alberta sets maximum permissible levels of gaseous air pollutants in the ambient air. No such standard is available for acidic precipitation. There is, at present, no integrated network in Alberta for the monitoring of acidic deposition (wet and dry) although independent, unrelated efforts for the measurement of precipitation and its chemistry are in progress in the Province.

9.3.1 Wet Deposition Effects on Agriculture

Exposure to simulated acidic precipitation resulted in reduced yields in 14 out of 19 agricultural species reviewed by Torn et al. (1987). However, there have been no field surveys documenting a reduction in yield due to ambient acidic deposition levels in the Province.

There is little evidence for a linear dose-response function for simulated acidic precipitation and plant injury. However, below pH 3.5, dose-response does approach linearity, with a yield loss of approximately 5% per decrease of one pH unit.

The formation, development, and survival of pods, flowers, and fruits are sensitive to simulated acidic rain at moderately low pH values (below 4.0). Foliar injury resulting from exposure to simulated acidic deposition can lower marketable yield of truck crops, lower plant resistance to pathogens, and has been linked with reduced plant productivity.

The threshold for simulated acid rain-induced foliar injury to agricultural crops was found to be between pH 3.0 and 3.5 for 36 crop species reviewed by Torn et al. (1987). In decreasing order (most to least) of sensitivity to simulated acidic precipitation, these crop types were: root, leafy, cole, legume, fruit, grain, and leafy and seed forage crops. The potential for economic loss was highest in leafy, cole, and fruit crops. Monocots such as wheat, barley, and timothy were found to be resistant to foliar injury from simulated acid rain above a pH of 2.5. At current

ambient levels of precipitation acidity there is little risk of foliar injury within the Province of Alberta; however, increased emissions may pose a risk to sensitive plants in the future.

Under the present conditions, it is unlikely that S or N in acidic deposition could be a significant source of foliar fertilizer to crops, or pose a risk of salt damage to crops in Alberta at current levels.

In summary, at current levels of precipitation acidity in Alberta, acidic wet deposition is not a concern for agriculture at this time.

9.3.2 Dry Deposition Effects on Agriculture

If the air quality standards for sulphur and nitrogen dioxide are met in the Province of Alberta, there should be no adverse effects on agriculture as a result of dry deposition under most conditions and with most species of agricultural plants. However, some studies reviewed by Torn et al. (1987) suggest that if the most sensitive agricultural species are exposed to sulphur dioxide at concentrations slightly higher than permissible standards under conditions conducive to gas exchange, they may be injured. To injure the most sensitive species, average SO_2 concentrations of 0.05 to 0.5 ppm for several hours are usually required. It is important to note that pollutant peaks are included within the average values. Thus, the avarage values do not represent the true exposure. The effects of ambient sulphur dioxide on the yield of agricultural crops are shown in Table 39.

Nitrogen dioxide concentrations of 0.25 to 0.50 ppm for long periods of time are generally required to induce injury in sensitive agricultural plants. However, a few studies have indicated injury to plants at concentrations at or below the maximum permissible Alberta concentrations. For this reason, Torn et al. (1987) believe that if the provincial standards are adhered to for acute nitrogen dioxide exposures, no injury should occur in agricultural species. A few experiments reviewed by Torn et al. (1987) did show plant injury under chronic exposure conditions at or above permissible concentration maxima. These authors questioned whether the standards for chronic exposure were sufficient to provide protection for sensitive agricultural species. The susceptibility or sensitivity to nitrogen dioxide exposure of a number of agricultural crop species commonly grown in Alberta is shown in Table 40.

Exposure to ozone concentrations of 0.03 ppm (for very sensitive species) and 0.10 ppm (for plants with intermediate sensitivity) for several hours is required to induce injury in agricultural plants. Research indicates that the maximum permissible concentrations for ozone specified under the Alberta Clean Air Act are sufficient to protect agricultural plants in the Province (Torn et al. 1987). Injury to agricultural species of intermediate sensitivity due to chronic exposures is generally not seen at long-term average ozone concentrations below 0.05 ppm (Torn et al. 1987). Agricultural crops grown in Alberta which are known to be relatively sensitive to ozone are shown in Table 41.

A review of the most recent research on the effects of hydrogen sulphide on agricultural crops indicates that present provincial standards are sufficient to protect plants (Torn et al. 1987).

Table 39. Effects of ambient sulphur dioxide on yield of various agricultural species.

Crop & Harvest Characteristics	Percentage of Control Value
Spring Canola (yield)	90.9
Alfalfa (yield)	81.0
Oats (yield)	76.1
Spring Wheat (yield)	73.4
Red Clover (yield)	63.6
Winter Rye (yield)	57.7
Winter Wheat (yield)	55.6

Exposure time: 4.3% of monitoring time

Concentration: 0.44 ppm - during exposure time*
0.083 ppm - average for monitoring time**

* The exposure time was calculated by summing all time intervals, Δt = 10 minutes, with a mean SO_2 concentration greater than or equal to 0.10 ppm.

** The monitoring time is essentially equal to the exposure time of the test plants.

Source: Guderian and Stratmann (1968)

Table 40. Susceptibility of various agricultural species which occur in Alberta to nitrogen dioxide.

Plant Species	Susceptible	Intermediate	Resistant
Alfalfa	+		
Annual bluegrass		+	
Barley	+		
Kentucky bluegrass			+
Oats	+		
Potato		+	
Red clover	+		
Rye		+	
Sweet corn		+	
Wheat		+	
Asparagus			+
Cabbage			+
Carrot[1]	+		+
Celery[1]	+	+	
Kohlrabi			+
Leek	+		
Lettuce	+		
Onion			+
Tomato		+	

[1]Different investigators reported different degrees of susceptibility

Adapted from the original table in Legge et al. (1980)

Source: National Academy of Sciences, U.S. (1977b)

Table 41. Agricultural crops grown in Alberta which are known to be relatively sensitive to ozone.

Alfalfa (*Medicago sativa*)
Barley (*Hordeum vulgare*)
Bean (*Phaseolus vulgaris*)
Red clover (*Trifolium pratense*)
Corn, sweet (*Zea mays*)
Grass, bent (*Agrostis palustris*)
Grass, brome (*Bromus inermis*)
Grass, crab (*Digitaria sanguinalis*)
Grass, orchard (*Dactylis glomerata*)
Muskmelon (*Cucumis melo*)
Oat (*Avena sativa*)
Onion (*Allium cepa*)
Potato (*Solanum tuberosum*)
Radish (*Raphanus sativus*)
Rye (*Secale cereale*)
Spinach (*Spinacea oleracea*)
Tomato (*Lycopersicon esculentum*)
Wheat (*Triticum Aestivum*)

Source: Hill et al. (1970)

Because injury to sensitive agricultural species has been observed during chronic exposures at or near maximum permissible levels of certain gaseous pollutants when present singly, there is concern over the possible more than additive effects of these pollutants at the same concentrations when present in combination.

More than additive, additive, and less than additive effects resulting in decreases in growth and yield have been observed with exposures to mixtures of SO_2 and O_3, SO_2 and NO_2, and NO_2 and O_3. In addition, researchers have found that in nearly every instance, exposure to a mixture of SO_2, NO_2, and O_3 causes a greater loss in plant growth and yield than the exposure to single gases or to mixtures of two gases. Growth and yield responses to nitrogen dioxide in pollutant mixtures occur in the nitrogen dioxide concentration range of 0.05 to 0.30 ppm. This is well below the current air quality standard and within the ambient concentration range of NO_2 within Alberta. The decrease in growth and yield caused by nitrogen dioxide in the presence of sulphur dioxide and/or ozone ranges from 5 to 20% at concentrations of nitrogen dioxide that cause little or no injury when the pollutant is present singly.

9.4. ALBERTA SOILS SENSITIVE TO ACIDIC DEPOSITION

Turchenek et al. (1987) provide a detailed overview of the soils of Alberta including their classification and the amounts of each major class in the province (Table 42), processes involved in soil formation and a general description of the major orders of the soils found in the province.

The sensitivity to acidic deposition of the various major soil classes is discussed at length by Turchenek et al. (1987) under three different approaches: soil sensitivity and mapping; qualitative descriptions of possible soil responses to acidification; and modelling approaches using dose-response methodology. Only the predictive model by Bloom and Grigal (1985) is described here; for other modelling approaches refer to Turchenek et al. (1987). The Bloom and Grigal (1985) model bases its predictions on two levels of acid input, (1) low - 0.1 Kmol (H^+) ha^{-1} y^{-1} and (2) high - 1.0 Kmol (H^+) ha^{-1} y^{-1}.

9.4.1 Soil Sensitivity and Mapping

Sensitivity refers to the ease with which soils can be affected or influenced by acidic deposition. Schemes for rating sensitivity of soils to wet and dry acidic deposition have been developed for the purposes of grouping geographic areas into sensitivity classes. The methods and parameters used to determine sensitivity vary according to the author and geographic region for which it was developed. In Alberta, Holowaychuk and Lindsay (1982) have developed such a system which was used to classify soil sensitivity in the Sand River area of northeastern Alberta (near Cold Lake). None of the systems in current use consider deposition impacts other than on pH and the exchange complex. Effects on organic matter turnover and on the dynamics of major nutrients such as N, P, and S are not considered. Insufficient data exist at the present time to incorporate impacts on organic matter and nutrients into the sensitivity classification systems in use. Therefore, these sensitivity ratings provide a first approximation of the potential impacts on some soil properties, and have been developed to identify specific soil types sensitive to acidic deposition and their locations.

Table 42. Areas of the soil orders in Alberta.[1]

Soil Order	Area (km^2 x 1000)
Chernozemic	141.5
Solonetzic	43.0
Luvisolic	203.1
Brunisolic and Podzolic	52.9
Regosolic	7.4
Gleysolic	21.6
Organic	104.6
Cryosolic	43.9
Nonsoil - Rockland, Icefields,	26.4
- Freshwater	16.8
Total	661.2

[1]Adapted from Holowaychuk and Fessenden (1987)

Holowaychuk and Fessenden (1986) have classified and mapped the soils of Alberta with respect to their sensitivity to acidic deposition. Soils of the province were described by delineating major soil landscape units and indicating the properties of both dominant and subdominant soils in each map unit. Mapping is on a broad regional scale resulting in inclusions and variation within soil groupings to be ignored. Attributes of soils used to differentiate map units include taxonomic class, pH, texture, and type of parent material.

9.4.2 Chernozemic Soil Impacts

Holowaychuk and Fessenden (1987) have identified the following Chernozemic soil types as being sensitive to acidic deposition: sandy, and some coarse loamy, Orthic Brown, Rego Brown, Orthic Dark Brown, Rego Dark Brown, Orthic Black, Rego Black, and Eluviated Black. In addition, a small area of Dark Brown soils in the Cypress Hills was indicated as being moderately sensitive. Summary statistics on Chernozemic soils in Alberta potentially sensitive to acidic deposition are presented in Table 43. The Chenozemic soils which appeared to be highly or moderately sensitive to acidic deposition are all slightly acidic to start with and are subgroups found on weakly to moderately calcareous parent materials.

Application of the Bloom and Grigal (1985) model to a few Alberta Chernozemic soils indicated that response to addition of about 0.1 kmol $(H^+)ha^{-1}\ y^{-1}$ and 1.6 kg S $ha^{-1}\ y^{-1}$ would be slight. Severe effects such as decline in pH and base saturation to the point of inducing aluminum toxicity would occur after about 200 years. A loading of 3 kmol $(H^+)ha^{-1}\ y^{-1}$ and 48 kg S $ha^{-1}\ y^{-1}$ would have drastic effects within 50 years in some soils of this group. Sandy soils of low CEC were found to be the most susceptible to acidification. Adverse effects were predicted to occur soonest in those soils which already have relatively low pH and base saturation levels.

An overriding issue in considering the effects of acidic deposition on Chernozemic soils is that most areas with such soils are under cultivation and are fertilized. The strong acidifying effects of fertilization are well documented and have been discussed elsewhere in this synthesis. In several reviews of this problem in recent years, it has been concluded that liming should become a general practice in order to restore productivity in lands affected by acidification due to fertilization practices. Any acidification caused by atmospheric deposition will thus be neutralized as well. Where liming practices are, in effect, soil responses to acidic deposition are not likely to be an important concern.

9.4.3 Solonetzic Soil Impacts

The area of Solonetzic soils in Alberta is about 42,960 km^2. None of these soils are presently regarded as being highly sensitive to acidic deposition, but about one-third are considered to be moderately sensitive (Holowaychuk and Fessenden 1987). Those which are relatively sensitive to acidic deposition are soils of the Solonetz great group which occurs on coarse parent materials or on shallow glacial deposits overlying residual materials. The Gray Solonetz subgroup is also in the moderately sensitive category because it lacks the Chernozemic type A horizons characteristic of prairie soils. The A horizon allows more leaching and lower colloid and base cation content in this horizon, thus lowering buffering capacity.

Table 43. Chernozemic soils sensitive to acidic deposition.

	Area (km^2)	% Sensitive	
		High	Moderate
Brown Chernozemic	34,306	16%	
Dark Brown	40,418	14%	
Black	2641	4%	<1%
Dark Grey	6848	52%	
Sandy/Coarse Loam	N.E.	All	

N.E. = No estimate

Adapted from Turchenek et al. (1987)

The Bloom and Grigal (1985) model was applied to two series of Solonetzic soils with low pH values (Camrose 4.8, Brownfield 4.9, measured as calcium chloride) using an acid input level of 0.1 kmol(H^+) ha^{-1} y^{-1}. At this low acid input level, the model predicted that for the tested soils series, only a minor lowering of pH and base saturation and increases in aluminum content would occur. The pH drop in 100 years was predicted to be approximately 0.2 units for the Camrose soil and 0.4 units for the Brownfield soil under high acid input levels of 1.0 Kmol(H^+) ha^{-1} y^{-1}; base saturation changes were also slight with Brownfield soils exhibiting the most decrease. The aluminum content was predicted to reach toxic levels in 250 years for Camrose soils and in 350 years for Brownfield soils.

Turchenek et al. (1987) also pointed out that although coarse Solonetzic soils were not addressed in the modelling, responses in pH, base saturation and aluminum content to acidic deposition would occur at a faster rate than the evaluated soils because of their texture. They predicted aluminum toxicity as a result of acid deposition would occur within 100 years.

9.4.4 Luvisolic Soil Impacts

The area of Luvisolic soils in Alberta is approximately 203,000 km^2. Most of these soils are considered to be moderately sensitive to acidic deposition with less than 5% being considered sensitive. Sensitivity is caused by a relatively low base status in the A horizon of Luvisolic soils. In addition, these types of soils are formed under forest vegetation. These soils, because of the inefficiency of nutrient cycling, may have low base saturation as well as low total exchange capacity.

The responses of five series of Luvisolic soils were evaluated using the Bloom and Grigal (1985) model. These were: Culp, Leith, Breton, Nosehill, and Tom Hill. The Tom Hill soil was a Podzolic Gray Luvisol and the Leith was a coarse Dark Gray Luvisol. All other test soils were Orthic Gray Luvisols which varied in texture, with the Breton and Nosehill being of the fine loamy variety and the Culp being coarse textured.

The modelling results for all test soils are shown in Table 44 for both high and low acid inputs. These predictions show pH depressions on all sub-groups tested at high acid inputs after 100 years. The most substantial changes occurred in the coarse textured Culp and the fine-loamy Tom Hill sub-groups. The model also predicted a small drop in base saturation in all sub-groups at low acid inputs. Base saturation at high acid inputs decreased, following similar trends to those detected for pH. For example, in the Culp sub-group, the model predicted base saturation to decrease from 87% to 44% within 100 years at the high acid input, while the least affected sub-group (Leith) indicated base saturation decreased from 89% to 70% within 100 years. Because of the higher clay and organic content of this latter sub-group, it has a higher CEC and exchangeable base content than the soils of the Culp series. Over the course of time all soils in the tested series were predicted to lose almost all of their base cations.

Aluminum content in the soils was predicted to increase only slightly at low acid inputs. Nosehill soils, the most acidic to start with, started with fairly high levels of aluminum (3 μM) which were predicted to rise to 9 μM within 100 years at high acid input. The model predicted increases in aluminum content to toxic levels for all soils over time. In a decreasing order of susceptibility to this predicted change

Table 44. Modelled predictions (Bloom and Grigal 1985) for soil pH responses to acid inputs.

Soil Type	Texture	Sub-Group	Sensitivity	Initial pH	Acid Input Level	Projected pH	Time Frame (Years)
LUVISOLIC			Moderate-High				
ORTHIC GRAY	Coarse	Culp	High	5.8	1.0	4.9	100
DARK GRAY	Coarse	Leith	Moderate	5.9	1.0	5.6	100
ORTHIC GRAY	Fine-loamy	Breton	High	5.6	1.0	5.3	100
PODZOLIC	Fine-loamy	Nosehill	High	4.4	1.0	4.0	100
ORTHIC GRAY	Fine-loamy	Tom Hill	High	5.4	1.0	4.7	100
BRUNISOLIC ELUVIATED DYSTRIC	Sandy	Firebag	High	5.1	0.1	4.6	100
				5.1	1.0	3.7	50
ELUVIATED DYSTRIC	Fine-loamy	Robb	High	4.2	1.0	3.7	50
				4.2	1.0	3.0	100
ORGANIC			High				NT
ORGANIC CYROSOLIC			Low				NT
GLEYSOLIC			Low				NT
REGOSOLIC			Low				NT

Acid input: High level 1.0 = 1.0 kmol (H^+) ha^{-1} y^{-1}
Low level 0.1 = 0.1 kmol (H^+) ha^{-1} y^{-1}

NT = Not tested

Adapted from: Turchenek et al. (1987)

in the aluminum concentration, the soils were: Nosehill, Culp, Tom Hill, Breton, and Leith.

The responses of Luvisolic soils to acidic inputs are generally similar to those of Chernozemic and Solonetzic soils. The response rates are highest in coarse textured soils with low CEC and exchangeable base content. The pH and base saturation in Luvisolic soils are relatively low. Therefore, critical levels of pH and aluminum content may be reached within shorter periods of time under acidic deposition than they would be in other soils.

9.4.5 Brunisolic and Podzolic Soil Impacts

About 40% to 45% of the 53,000 km^2 of Brunisolic soils in the province are considered to be highly sensitive to acidic deposition (Holowaychuk and Fessenden 1987). These soils are mainly Eluviated Eutric Brunisols and Eluviated Dystric Brunisols developed on glaciofluvial and eolian deposits. Other types of Brunisols in the Province have a low sensitivity to acidification. A small area of about 390 km^2 of Orthic Humic Podzols and associated Dystric Brunisols occurring west of Grande Cache are also rated as being highly sensitive to acidic deposition (Holowaychuk and Fessenden 1987).

The modelled predictions (Bloom and Grigal 1985) for two sensitive soils of this group are shown in Table 44 for both high and low acid inputs. The Firebag soils were predicted to have a strong response to low level acid inputs with effects beginning to show within 100 years. This response was the highest for all the soils tested using the Bloom and Grigal (1985) model. Along with the observed pH depression, the base saturation of Firebag soils dropped from 31 to 10% and aluminum content increased from 0.9 to 2 µM at low acid inputs. Both soils tested were predicted to react drastically to high acid inputs with pH and base saturation dropping substantially and aluminum content rising within 50 years. The calculated aluminum content for both soils was predicted to be over 100 µM within 50 years, an alarmingly toxic level. Although the initial aluminum content of these soils is not known, it is suspected to be in the order of 10 µM for the Robb soil and less than that concentration for the Firebag soils. Therefore, the predicted rise is dramatic.

The acid deposition response simulations indicate that sandy Brunisolic soils are among the most sensitive in Alberta and that particular attention should be given to these soils and the ecosystems they are associated with. Finer textured Brunisols are considered to be less sensitive, but the simulations indicate that there could be problems related to high aluminum in soils of very low pH. It should be noted, however, that although high aluminum contents were predicted for the sandy Firebag soils, the lack of easily weatherable minerals in these soils may not allow the system to contribute the high aluminum levels predicted.

9.4.6 Organic and Organic Cryosolic Soils

Almost all of Alberta's 104,500 km^2 of Organic soils are considered to be highly sensitive to acidic deposition (Holowaychuk and Fessenden 1987). Organic soils throughout the Province are generally in the very strong to medium range of response to acidity, have low base saturation, and on a volume basis, low base status. If subjected to further acid inputs, the pH would be reduced and further depletion of base saturation would occur.

The 43,000 km^2 of Organic Cryosols in the Province are rated as having low sensitivity to acidic deposition (Holowaychuk and Fessenden 1987). Most Organic Cryosols are highly acid in reaction and it is generally conceded that additional acid will not cause further acidification or alter their base status.

The soil response simulation model was not run for either Organic or Organic Cryosol soils. The Bloom and Grigal model was developed for use on mineral soils and was not considered applicable to organic soils because model input parameters such as pH-base saturation relationships, and aluminum activity coefficients, differ between organic soils and mineral soils (Turchenek et al. 1987).

9.4.7 Gleysolic Soil Impacts

There are about 21,000 km^2 of Gleysolic soils in Alberta. These have been rated as having low sensitivity to acidic deposition (Holowaychuk and Fessenden 1986). A small 836 km^2 area northeast of Grande Cache is the only exception, and is rated as having a high sensitivity. No acidity response simulation was run for this type of soil because of its lack of sensitivity (Turchenek et al. 1987).

9.4.8 Regosolic Soil Impacts

There are approximately 7400 km^2 of Regosolic soils in Alberta. They are not considered to be sensitive to acidic deposition because they receive continuous replenishments of calcareous materials by means of alluvial sedimentation. Most of these soils are found in the Peace-Athabasca Delta. No acidity response simulation was run for this soil type because of the suggested lack of sensitivity to acidification.

9.4.9 Impacts on Rocklands and Rough-Broken Lands

Rockland and Rough-Broken Lands account for about 35,000 km^2 of Alberta's land area. Two groups of these lands are considered to be sensitive to acidic deposition, the Precambrian Shield area of northeastern Alberta and Cordilleran areas of almost barren clastic sedimentary rock and mineral materials. Coarse textured Brunisolic and Podzolic soils occur within the Rockland areas.

9.5 EFFECTS OF ACIDIC DEPOSITION ON SOIL MICROORGANISMS AND PROCESSES

The majority of studies dealing with the impact of acidic deposition on qualitative and quantitative aspects of the soil microbial community have dealt with chronic effects in the field and, therefore, the results may be applicable to some Alberta soils. It can be concluded that acidification of a naturally acidic forest soil (in Alberta, the pH of surface soils in many coniferous forests ranges from 4.6 to 6.0) to approximately pH 3.0 or less, results in a significant reduction in total microbial biomass. Bacteria are adversely affected at pH 4.0, and fungi appear to be less sensitive to acidification.

Factors in the N cycle such as ammonification, nitrification, nitrogen fixation, and symbiotic relationships are especially sensitive to acidity and could be adversely affected by acidic deposition. There is little reduction in the rates of ammonification until the pH reaches 3 or less but nitrification and nitrogen fixation are inhibited in soils below pH 6. It appears clear that the legume-*Rhizobium* symbiosis is acid sensitive.

Although studies concerning the relationship of acidic deposition and mycorrhizae are few in number, they indicate that these symbiotic relationships are largely resistant to chronic exposures. Most ectomycorrhizal plants are associated with a diverse array of acid tolerant fungi which probably provide a strong environmental cushioning capacity against chemical change. In possible contrast, at least some VA mycorrhizal fungi are acid sensitive. Reductions of pH by 0.5 to 1 unit may render certain of these species nonfunctional with consequential reduction in plant growth.

Most of the laboratory simulation studies reviewed by Visser et al. (1987) used extremely low pH levels that did not occur in ambient conditions. Because of this, these studies are not considered relevant to the provincial problem. However, based on a review of both laboratory and field studies by these same authors, it is clear that a reduction in the pH of naturally acidic forest soils to 3.0 or less will have an inhibitory effect on soil respiration. However, the high buffering capacity of litter and decaying plant residues and the probable presence of microbial flora adapted to acidity in such situations makes it likely that extremely high dosages of acidic rain or sulphur dioxide would be necessary to reduce microbial respiration to any substantial degree. It is not known if this would also be the case in agricultural grasslands where less acid tolerant microflora may reside.

Controlled laboratory and field experiments have also shown that simulated acidic rain of pH 2.0 or fumigations with sulphur dioxide up to 530 ppb are necessary to inhibit litter decomposition. It is unlikely that either situation will ever occur in Alberta under present conditions or if current environmental standards are maintained.

9.6 SULPHUR MICROBIOLOGY IN THE ALBERTA CONTEXT

The review of soil sulphur microbiology prepared by Laishley and Bryant (1987) is of particular relevance to Alberta. The topic deals with elemental sulphur breakdown and bears direct relevance to soils and soil acidity because of the importance of the sulphur industry in the Province and the storage of sulphur and fugitive sulphur dust problems associated with it.

Only key highlights of the Laishley and Bryant (1987) report will be presented here:

1. The sulphur oxidizing colourless bacteria and particularly the thiobacilli are the principal microorganisms responsible for the breakdown of elemental sulphur in Alberta.
2. Biological oxidation of inorganic sulphur can create acid soils, with accompanying leaching of nutrients such as Fe^{2+} and Al^{3+}, resulting in toxicity to plants. Bacterial acid production can also cause direct injury to plants.
3. Different microorganisms can oxidize sulphur at different rates. The most prolific oxidizers belong to the genus Thiobacillus, different species of which oxidize sequentially as acid conditions in the soil change under oxidizing conditions created by the bacteria themselves (Laishley and Bryant 1987).

4. Factors affecting the oxidation of fugitive (wind blown) sulphur include:
   a. the particle size and microcrystalline structure of the sulphur itself;
   b. the types of sulphur oxidizing bacteria present at the deposition site. For example, the acidophilic thiobaccilli would not be active in soils with basic pH. Conversely, in more acidic environments, it would be unusual to find less acidophilic bacteria playing a dominant role. Oxidation processes can also be limited by the formation of biofilms of bacteria on the upper molecular layer of sulphur particles (Bryant et al. 1983). These films, formed of bacterial cells and colonies and their attachment glycocalyx, effectively seal off the sulphur to continued oxidation (Takakawa et al. 1979; Costerton and Irvin 1981; Ladd 1982; and Bryant et al. 1983);
   c. the soil environment. Bryant et al. (1985) have shown that bacterial oxidation process decreases with temperatures above or below the optimum of 28°C. They also found that temperatures of 5°C or 37°C effectively stopped sulphur oxidation by Thiobacillus albertis. The bacteria were reactivated if temperatures were increased above 5°C but died at 37°. This information is important to the Alberta situation because it suggests that to minimize sulphur oxidation, the sulphur should be kept cool. Alberta is noted for its long winters and cool overall climate which should assist in reducing oxidation rates. All bacteria known to oxidize sulphur in Alberta are capable of withstanding freezing, and reactivating when warmer conditions return (Laishley and Bryant 1987).

      Soil type, especially pH, texture, and base saturation, has also been shown experimentally to affect bacterial oxidation of sulphur (Laishley and Bryant 1987). The percentages of soils in Alberta with pH less than 6.0, based on soil testing data, are shown in Figure 11.

      The third soil factor determining the rate of sulphur oxidation by bacteria is the moisture and nutrient status of the soil. Thiobacilli are aerobic and will not grow in waterlogged soils (Laishley and Bryant 1987). Laishley and Bryant (1985) have also shown that under dry soil conditions, sulphur oxidizing activity was low. What is required for bacterial oxidation is a level of moisture close to, but not exceeding, soil moisture holding capacity. Microorganisms require the same nutrients as plants for successful growth. Sulphur oxidation, in fact, may be enhanced by N-P fertilization (Bloomfield 1967) which suggests that agricultural soils in Alberta associated with gas plants may have high sulphur oxidation.

5. Fugitive (wind blown) sulphur from existing stock piles or sulphur operations will create an ideal soil environment for the sulphur oxidizing Thiobacilli, with the end result being acidification of the soil. Long term studies of SO_2 contamination of soils near a gas plant source did not show trends in acidification (Lore 1984). This finding suggests that

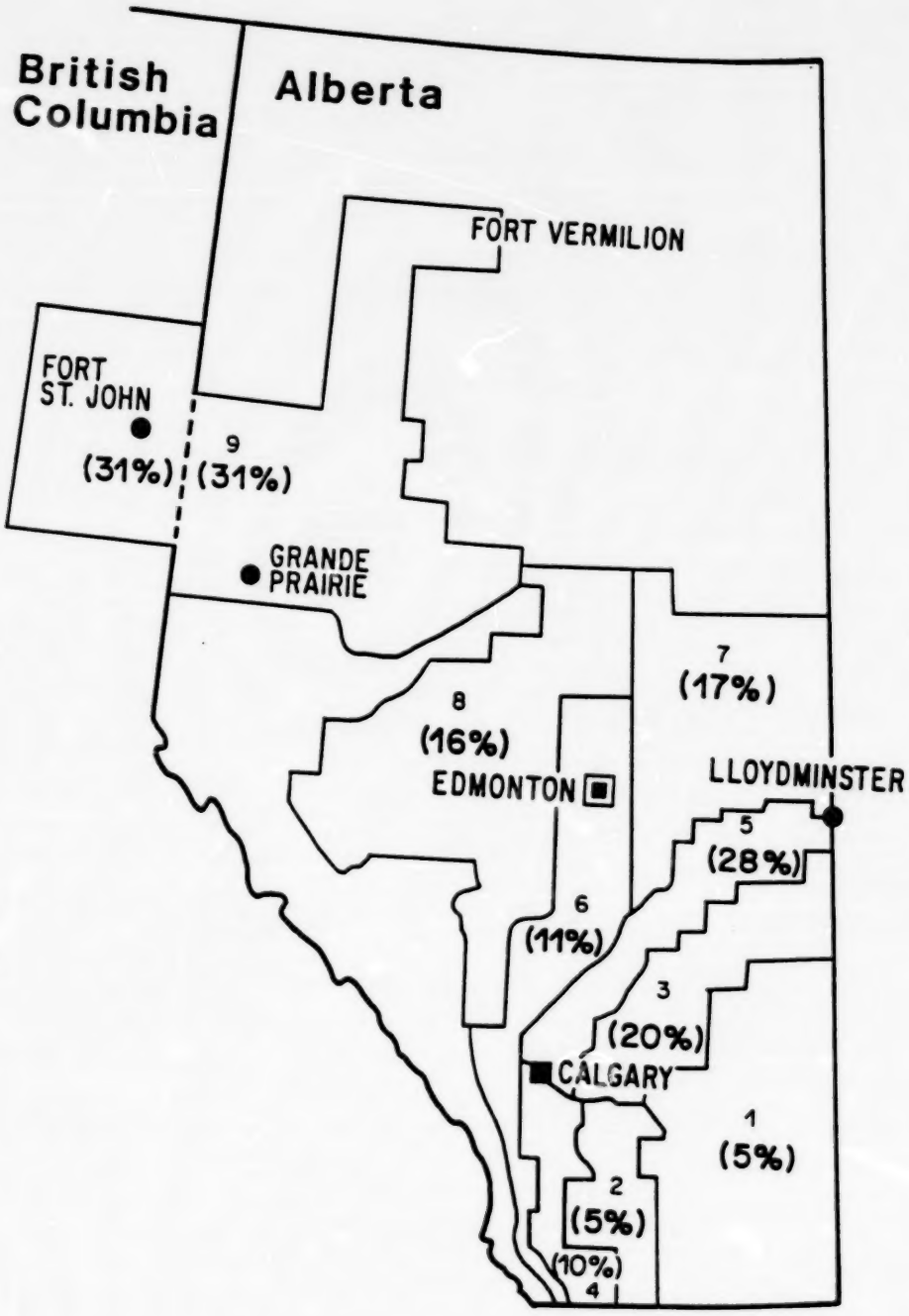

Figure 11. Location of soil testing areas in Alberta, and the percentage of cultivated soil with a pH of 6.0 or less for each area. (Taken from Penney et al. 1977)

acidification of soils from sulphur dioxide deposition is not as severe a problem in Alberta as wind blown elemental sulphur dust.

Liming of acid soils polluted with sulphur only masks an existing problem and really provides a more favourable environment for continued microbial sulphur oxidation and acidification (Laishley and Bryant 1987). Reports by Nyborg and Hoyt (1978) and Ivarson (1977) indicate that liming causes a temporary increase in organic nitrogen mineralization but also results in an increase in microbial activity. Increasing the nutrient status of such soils while leaving the elemental sulphur as a microbial substrate will tend to favour continued oxidation by thiobacilli and, hence, renewed acidification. This means that the original reason for the liming will reoccur quickly unless the sulphur is removed.

6. Decommissioning of sour gas plants and recovery of bulk sulphur storage blocks are becoming more commonplace in Alberta. Unfortunately, many of the sulphur blocks were laid directly on bare soil and it is estimated that there may be 20% to 30% of the sulphur left in the soil at the end of the cleanup process (Hyne, pers. comm. in Laishley and Bryant 1987). These soils will be subject to intensified microbial acidification processes, particularly if the remaining sulphur is in powdered form.

9.7 SURFACE WATER ACIDIFICATION STUDIES IN ALBERTA

Hesslein (1979) surveyed 20 lakes in the Alberta Oil Sands Environmental Research Program (AOSERP) study area near Fort McMurray in order to determine their susceptibility to pH change resulting from acidic deposition. The lakes were sampled for only a short period of time; October 6 - 10, 1976. Most lakes in the region were found to have high pH values and high alkalinity. However, lakes could be divided into two groups: (a) pH and alkalinity in the range of 6.18 - 7.49 pH units and 342 - 811 $\mu eq\ L^{-1}$, respectively, and (2) pH and alkalinity in the range of 7.89 - 8.32 pH units and 965 - 3090 $\mu eq\ L^{-1}$, respectively. The first group of lakes is located at the northwest corner of the study area, whereas the second group of lakes is located in the more alkaline region along the Athabasca River. Hesslein (1979) suggested that the first group of lakes might be susceptible to serious pH alterations if the average pH of rain is below 4.0. However, this is unlikely to happen. Sulphur emissions in Alberta are controlled by provincial legislation, allowing less than one percent of the total oxides of sulphur to be emitted into the atmosphere. The Sudbury, Ontario area, with much greater emissions of sulphur dioxide than Alberta, has an average precipitation pH of 4.0 to 4.5. Thus, it is unlikely that precipitation pH of less than 4.0 could occur in Alberta (Hesslein 1979).

Erickson and Trew (1987) compiled historical water chemistry data for 875 lakes throughout Alberta. In addition, 107 lakes from the northern part of the Province were surveyed and water quality data were collected. The study was designed to identify the sensitivity of lakes to acidification. Based on earlier Canadian studies, the following parameters were measured or compared in each lake: pH, calcium, and alkalinity. The results of the study are shown in Table 45. Based on these findings, Erikson and Trew (1987) suggested that lakes in widely diverse areas of the province are potentially

Table 45. Indicator parameters used to classify the sensitivity to acidification of Alberta lakes.

Parameter	Range	% of Surveyed Lakes in a Range Sensitive to Acidification
pH	3.4 - 10.6	17
Calcium (mg L^{-1})	0.1 - 8.0	18.6
Alkalinity (mg L^{-1})	Undetected - 7772	9.7

Adapted from: Erickson and Trew (1987)

sensitive to the effects of acidic deposition. A large number of sensitive lakes are located on the Canadian Shield in the northeastern part of the Province. Several other sensitive lakes were detected in the Rocky Mountains and in particular, Jasper National Park. The northern upland areas of Clear Hills, Swan Hills, Caribou and Birch Mountains also contain lakes which, based on the survey results, indicate potential sensitivity to acidic deposition. A number of these lakes appeared to be naturally acidic based on their colour and muskeg drainage characteristics.

In Alberta, streams and rivers have been routinely sampled by Environment Canada and Alberta Environment since 1969. Very few lakes, particularly the ones at high altitudes, have been sampled by either agency. In general, most Alberta rivers and streams have high pH values (above 7.5) and high alkalinity (above 1000 $\mu eq\ L^{-1}$) (Environment Canada 1982).

Most of Alberta, except the northeast corner of the province, is underlaid by carbonate rich minerals (limestone, dolomite, slightly calcareous rocks) with medium to high buffering capacity. The northeast corner of the province is in the Precambrian Canadian Shield and is underlaid by granitic gneisses and quartz sandstone with low buffering capacity. Shewchuk (1981) conducted regional surveys of rain, snow, and lake water chemistry in several locations on and near the Precambrian Shield of western Canada. The areas surveyed included part of Saskatchewan (east to northwest section), part of Manitoba, The Northwest Territories, and the northeastern section of Alberta. Snow and rain in the region exhibited average pH values of 5.0 and 6.4, respectively, indicating that the area was not receiving significant amounts of acidic deposition. The pH of lakes on the Precambrian Shield averaged 7.3; the pH of lakes on the fringe or off the Precambrian Shield averaged 8.1. Sulphate, alkalinity (as $CaCO_3$), and calcium ion concentrations in the Precambrian Shield averaged 2.7, 13, and 4.3 mg L^{-1}, whereas, in the fringe or off-shield lakes the average was 15, 200, and 55 mg L^{-1}, respectively. Although Precambrian Shield lakes are highly sensitive to acidic deposition due to lack of buffering capacity, there is little evidence to suggest that at present they are undergoing significant acidification. Acidification studies conducted on lakes located in the Precambrian Shield of Nova Scotia, Ontario, and Quebec, however, suggest that these lakes have become acidic over the last few decades. Acidic deposition is reported to be the cause of the lake acidification. Although the mechanism of their acidification is a subject of much discussion, it appears that lakes located in this sensitive Shield area are susceptible to acidification. Therefore, one can make a cautious prediction that lakes located in the northeast corner of Alberta may also be susceptible to acidification.

Three reports coordinated by Alberta Environment and Western Canada LRTAP (Long Range Transport of Air Pollutants) concerning the acidification potential for northern Alberta are nearing completion. They include: an inventory of freshwater systems and their sensitivity ratings; a mapping of the northern soils and hydrogeology; and, a statement of target loading for northern Alberta (David Trew, Alberta Environment, personal communication cited in Telang 1987). When completed, they will provide a valuable tool for examining future scenarios of, and possible mitigative measures for, aquatic acidification in northern Alberta, particularly in the context of oil sands production and development.

9.8 ALBERTA HYDROGEOLOGY AND GEOLOGY

In Alberta, groundwaters are characterized by relatively high pH values (6.5 to 8.0) and high acid neutralization capacities. Although groundwater chemistry data in the northern part of the Province are limited, Schwartz (1979, 1980) suggested that even in muskeg areas, groundwater is characterized by pH values in the 6.5 to 8.0 range.

Much of Alberta is covered with relatively thick deposits of glacial till that have high acid neutralization capacity. It is doubtful if acidification of groundwater in these deposits would occur in the short term given the present level of atmospheric loading. It may, however, be possible to see the residues or byproducts of the acid neutralization process in selected aquifers.

Krouse et al. (1984) have found evidence in the West Whitecourt area to suggest that the products of acid neutralization reactions have already begun to reach the water table.

Aquifers in Alberta which are most likely to show some documentable response to acidic deposition would be characterized by:

1. low buffering capacity;
2. rapid recharge;
3. shallow, short flow regime; and
4. high permeability.

Geological settings that are likely to reflect the above-mentioned hydrogeological characteristics would occur where aeolian or glaciofluvial deposits overlie dense low permeability till or bedrock.

Groundwater resources in Alberta are utilized extensively for domestic, agricultural, municipal, and industrial purposes. Changes in groundwater as a response to acidification could have a dramatic effect on the economy and public health of the Province. Experiences in other parts of the world, such as Sweden, coupled with the evidence cited from Whitecourt (Krouse et al. 1984), should alert Albertans that even in our well protected environment, the potential exists for acidity-induced effects to be felt in our groundwaters.

9.8.1 Geological Information Bases for Alberta

9.8.1.1 Bedrock Geology. As part of his review of the geological and hydrogeological aspects of Alberta pertaining to acidic deposition, Campbell (1987) compiled a 1:1,000,000 scale bedrock geology map of the Province. This map was based on information contained in maps compiled by Green (1972). Included in the Campbell map sheet are data covering the area and types of bedrock, and metal formations within the Province. These data are essential for the determination of bedrock and groundwater sensitivites to acidic deposition.

9.8.1.2 Surficial Geology. Campbell (1987) has also compiled a 1:1,000,000 scale surficial geology map of Alberta. This map was based on information assembled from the following sources: Geology Branch of the Research Council of Alberta, Geological Survey

of Canada, the Exploratory and Reconnaissance Soil Survey of Alberta Research Council, and Special Geomorphic Landforms Maps (Environment Canada and Alberta Energy and Natural Resources, Parks Canada Biophysical Inventory, and the Atlas of Alberta 1969). This inventory is critical because of the effects that surficial materials have on shallow groundwater chemistry and soils acidification processes.

9.8.2 Hydrogeology Resource Inventory

Mapping of the hydrogeological resources has been completed for the Province by the Alberta Research Council. Groundwater chemistry varies markedly in Alberta, because of the differences in geology, topography, climate, vegetation, and soils (Campbell 1987). The Hydrogeological Maps of Alberta contain regional information on the chemistry of groundwater but these are often from isolated samples taken during water well installation, logging or during soils surveys, for example. There is at present no systematic groundwater sampling network to monitor groundwater chemistry in the Province.

9.9 SULPHUR ISOTOPE STUDIES IN ALBERTA

The following discussion was extracted from the review by Krouse (1987) on "Sulphur isotope studies in Alberta in reference to acidic deposition".

Environmental sulphur isotope studies have been conducted in Alberta since the late 1960's. To date, thousands of analyses have been carried out for sulphur compounds on samples from the atmosphere, hydrosphere, pedosphere, and biosphere. From the viewpoint of using stable isotopes to trace pollutant sulphur (S) in the environment, Alberta is one of the few places in the world where industrial emissions differ greatly in isotopic composition from those of the preindustrial environments. Consequently, these investigations have not only served to identify and trace industrial S at locations in Alberta, but have contributed immensely to our understanding of fundamental concepts concerning uptake and utilization of sulphur by environmental receptors.

The importance of sulphur isotope studies in environmental research is that stable isotope abundances can usually provide information on the source of sulphur pollutants. Very few other analytical techniques have this capability. Conventional measurements of pollutant concentrations fail to apportion sources. Cases can be cited where high concentrations of sulphate have been wrongly attributed to a specific industrial source as a result of conventional analyses.

Basic principles of stable isotopes which pertain to sulphur pollution include the following:

1. Isotopes of an element differ in their masses. Since many processes are mass dependent, the relative abundances (the ratio of the number of ^{34}S atoms to ^{32}S atoms) in natural components are altered.
2. In nature the process which alters sulphur isotope abundances most significantly is bacterial SO_4^{2-} reduction during which $^{32}SO_4^{2-}$ is converted faster than $^{34}SO_4^{2-}$ to sulphide.
3. Sulphur pollutants usually differ in isotopic composition from their environmental receptors.

4. On the basis of (3), the presence of pollutant sulphur in the environment, and often the ratio of pollutant-to-natural sulphur, may be determined.
5. Successful isotope tracing of pollutant sulphur requires minimal isotope fractionation during transport and deposition. This criterion is difficult to meet in anaerobic environments because of bacterial reduction processes. However, most studies of the atmosphere, water, and soil involve aerobic conditions where the following processes have minimal isotopic selectivity:
   a. chemical or bacterial oxidation. Addition of oxygen does not greatly influence the sulphur isotope composition.
   b. high temperature processes, e.g., in power plant stacks. Isotope fractionation decreases with increasing temperature.
   c. SO_4^{2-} assimilation by bacteria or plants.
   d. reactions of sulphur compounds in the solid state, such as dissolution of evaporites or oxidation of elemental sulphur. The reaction proceeds essentially layer by layer, thus limiting isotopic selectivity.
   e. conversions among larger complex molecules if bond rupture involves large fragments of the molecule. In that case, isotopic substitution does not produce a large percent change in mass in the species undergoing reaction.
6. An exception to the above principles is the isotopically selective emission of reduced sulphur compounds by vegetation under stress. Therefore, enrichment of heavier sulphur isotopes in vegetation to levels above those of known sources can serve as a stress indicator.
7. Since the uniform isotope composition of O_2 in the atmosphere differs greatly from the variable isotopic composition of water, oxygen isotope measurements of sulphate provide information concerning the oxidation of pollutant sulphur.
8. Isotopic data should be considered as a complementary rather than an alternate tool. With the exception of the emission of reduced sulphur compounds by stressed vegetation, isotope data alone do not relate environmental impacts to sources. They must be used in combination with biological data.
9. Isotope data are most effective when background measurements are taken prior to commencement of an industrial operation. This is seldom the case. However, it is often possible to estimate the background conditions. Further, it is useful at any time to establish an isotopic "baseline" with which future measurements might be compared.

Further isotopic data may identify an important phenomenon which is not discernible from conventional concentration data. For example, unusual enrichments of the heavier ^{34}S in foliar S are consistent with isotopically selective emissions of reduced S under environmental stress. The concentrations of S alone in foliage would not provide evidence of this biochemical reaction.

Studies in Alberta using isotopes as tracers have significantly advanced global investigations of anthropogenic S in the environment. These studies have been summarized in Fritz and Fontes (1980) and Tabatabai (1986). A review of these studies was long overdue and, therefore, much of the review by Krouse (1987) contains data from many studies that have not previously been published. A summary of the principal findings gleaned from many of the Alberta studies is provided below:

1. Hydrogen sulphide released to the atmosphere from springs in the Rocky Mountains of Alberta is depleted in the heavier sulphur isotopes as the consequence of bacterial SO_4^{2-} reduction (Krouse et al. 1970).
2. The first study of sulphur isotope abundances in soils revealed $\delta^{34}S$ values* near $0^{o}/_{oo}$ in central Alberta and as low as $-30^{o}/_{oo}$ in the Peace River area (Lowe et al. 1971). $\delta^{34}S$ values near $0^{o}/_{oo}$ have since been found for soils in many locations, e.g., Ram River (Krouse 1977b) and West Whitecourt study area (Krouse et al. 1984). Very negative values have been found at Teepee Creek (Krouse and Case 1981) and near small lakes in the Twin Butte area.
3. Dissolved sulphate in the Mackenzie River system was found to vary in sulphur isotope composition over almost the total range encountered globally for fresh water. Rivers draining the Peace River area have SO_4^{2-} with highly negative $\delta^{34}S$ values consistent with soils data for that region (Hitchon and Krouse 1972).
4. In contrast to the above, sour gas (H_2S-rich) in carbonate reservoirs of Alberta has quite positive $\delta^{34}S$ values (Krouse 1977a).
5. The air in Alberta near sour gas plants tends to have SO_2 enriched in ^{34}S (i.e., positive $\delta^{34}S$ values) in comparison to the global average.
6. Ground level SO_2 near Crossfield, Alberta became more enriched in ^{34}S as the sour gas processing plant went from shutdown to full production. The $\delta^{34}S$ value ($+29\ ^{o}/_{oo}$) of the stack gas was mathematically predicted from the ground level data and experimentally verified using a helicopter mounted high volume sampler (Krouse 1980).
7. Effects of wind direction on the isotopic composition of SO_2 reaching a monitoring site were documented in the West Whitecourt Case Study (Krouse et al. 1984). A wind-direction activated array of high volume samplers was used.
8. The presence of sulphur of industrial origin was documented isotopically in surface waters near sour gas processing plants, e.g., Valleyview (Krouse and Case 1983) and the West Whitecourt study area (Krouse et al. 1984).
9. A correlation was found between the sulphur isotope composition of SO_4^{2-} and the dissolved organic S content in surface waters in the West Whitecourt case study, indicating that industrial S interacted with organic matter in the environment (Krouse et al. 1984).

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* see Krouse (1987), p.8, Figure 3

10. In the Calgary river system, lateral mixing of SO_4^{2-} is slow. Different sources of effluents identified by a cross-sectional isotopic study is a possibility that has been suggested by Krouse (1980).
11. Random sampling in the Ram River area over two years showed that epiphytic lichens had a $\delta^{34}S$ distribution similar to atmospheric SO_2 (Krouse 1977b).
12. Lichens in the Fox Creek area had higher $\delta^{34}S$ values in locations more exposed to SO_2 emissions; those on the lee side of hills had lower values than those exposed on the windward side (Case and Krouse 1980).
13. In contrast to statement 11, conifer needles had $\delta^{34}S$ values intermediate to those of atmospheric SO_2 and the soil. This demonstrated that foliage could acquire sulphur from the atmosphere as well as by translocation from the root system (Krouse 1977b). This phenomenon has been verified by several other investigators (Krouse 1987).
14. Foliar uptake of sulphur from the atmosphere and soil was demonstrated isotopically in the field with potted plant experiments conducted by Winner et al. (1978).
15. The sulphur isotopic compositions of mosses were found to vary with downwind distance and direction near a sour gas plant in the Fox Creek area. Higher $\delta^{34}S$ values corresponded to closeness to the source of emissions (Winner et al. 1978).
16. Ground lichens and mosses appeared not to be as enriched in ^{34}S as those on trees in the same area, e.g., Brazeau (Latonas et al. 1986).
17. Moss was found capable of trapping atmospheric S compounds, thus preventing their transport to the subsoil (Krouse 1980). Litter generally is capable of blocking the downward movement of wet and dry deposition of S-compounds (Legge et al. 1986).
18. Conifer needles may display more positive $\delta^{34}S$ values with increasing height on a given tree (unpublished data, Ram River 1972; Krouse et al. 1984). This can be explained because upper branches exert a canopy resistance resulting in the exposure of lower branches to reduces S. concentrations (Lester et al. 1986).
19. Consistent with statement 18, the needles on the uppermost branches of lodgepole pine were found to be unusually enriched in ^{34}S compared with those lower in the canopy (Krouse et al. 1984).
20. Some lichens in the Fox Creek area had unusually high $\delta^{34}S$ values, suggesting that under sulphur stress, gaseous compounds depleted in $\delta^{34}S$ were emitted by the lichens (Case and Krouse 1980).
21. Laboratory experiments showed that H_2S was emitted by cucumber plants grown in high concentrations of SO_4^{2-} and HSO_3^-. The H_2S was depleted in ^{34}S by as much as 15‰, compared with the nutrient solutions (Winner et al. 1981).

22. In the Ieepee Creek area of Alberta, sulphur isotope data revealed that foliage and soils with high sulphur contents were associated with shallow subsurface sulphate mineral deposits. These natural sulphur sources, quite depleted in ^{34}S, dominated the environmental sulphur cycle in that area (Krouse and Case 1981).
23. Sulphur isotope analyses of soil cores near Valleyview, Alberta were used to document penetration of sulphur of industrial origin into the subsoil in the vicinity of a flare stack which had been operational for over two decades (Krouse and Case 1983). Data for the West Whitecourt study area showed subsoil movement of sulphur of industrial origin (Legge et al. 1986).
24. At Ieepee Creek, soil texture was found to be an important factor with clay particles retaining S-compounds to a greater extent than sand (Krouse and Case 1983).
25. Other factors influencing the penetration of industrial S into the subsoil are vegetation cover (Statement 17), duration of emissions, and hydrology (Krouse et al. 1984).
26. In soil profile studies, isotope data revealed that sampling by horizon is more meaningful than sampling pre-selected depth intervals.
27. Sulphur isotope data from the Zama area and elsewhere strongly suggest that in rolling terrain, sulphate minerals accumulating in depressions may contribute to visible stress symptoms on vegetation, whereas plants on knolls may be growing in S-deficient soil. The latter may display the isotopic signature of industrial emissions and may actually be utilizing available atmospheric sulphur (Krouse and Case 1982).
28. As sulphur is passed through the food chain, the isotopic discrimination is minimal, i.e., animals have a sulphur isotope composition similar to their diets. Citizens of Calgary were found to have remarkably consistent $\delta^{34}S$ values (near $0^{o}/_{oo}$) in their hair, nails, blood, kidney stones, and urine.

9.10 ACIDIC DEPOSITION IN THE ALBERTA CONTEXT: LITERATURE CITED

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